Metal containing polysiloxane derivatives as catalysts

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METAL CONTAINING POLYSILOXANE DERIVATIVES

AS CATALYSTS

A Thesis submitted by Roy G. Phillipps

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TO INGRID

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Summary

Organofunctionalised model siloxanes of general formula $Me_3SiO[MeSi(R)O]_nSiMe_3$ (n = 1, 2, 3, R = $CH{=}CH_2$; n = 1, R = $-CH_2CH_2PPh_2$, $-CH_2CH_2SPh$ and $-CH_2CH_2SBu$) and linear polysiloxanes of general formula $Me_3SiO[Me_2SiO]_x[MeSi(R)O]_ySiMe_3$ (R = -H, $-CH{=}CH_2$, or alkyl chains terminated by $-CH{=}CH_2$, $-NHCH_2CH_2NH_2$, $-C_6H_9$, $-C_6H_5$, -SPh, $-PPh_2$ and $-SCH_2COOH$ entities) have been prepared and characterised. Trisiloxanes containing S and P donor centres were prepared from $Me_3SiO[MeSi(CH{=}CH_2)O]SiMe_3$ by photochemical addition of HSR and $HPPh_2$ respectively, whereas polysiloxanes were prepared by either acid or base catalysed equilibration of $(Me_2SiO)_4$ and $Me_3SiO(Me_2SiO)_nSiMe_3$ (n = 0, 1 or 2) with a suitably functionalised linear or cyclic siloxane. Subsequent chemical modification of polysiloxanes containing $-CH{=}CH_2$ or $-(CH_2)_4CH{=}CH_2$ functionalities yielded $-PPh_2$ and -SR containing analogues.

A selection of the model organosiloxanes and organopolysiloxanes have been metallated with a range of transition-metal entities which include $M(CO)_4$ (M = Mo, Cr, W), MCl_2 (M = Pt, Pd, Co, Ni, Cu), $M(BF_4)_2$ (M = Pt, Pd, Co, Cu, Ni), RhCl, $Rh(CO)_2Cl$, Rh(CO)Cl, Ru(OAc)Cl and $M(OAc)_2$ (M = Co, Cu, Ni).

The metallated and non-metallated siloxanes have been characterised where practicable and appropriate using ^{13}C, ^{1}H and ^{29}Si nuclear magnetic resonance spectroscopies, gel permeation chromatography, infrared and electronic absorption spectroscopies and elemental analyses.

A selection of the metallated model siloxanes and polysiloxanes have been tested for catalytic activity. In the hydrosilylation reaction of 1-decene with $(Me_3SiO)_2Si(Me)H$, platinum and rhodium metallated phosphine functionalised siloxanes were found to provide the most

active catalysts, with reactions generally being complete after 15 - 20 minutes at 110°C. The oxidative coupling reaction of 2,6-disubstituted phenols catalysed by Cu-, Co- and Ni(II) species bound to $-(CH_2)_3NH(CH_2)_2NH_2$ functionalised polysiloxanes has also been briefly examined. For this process supported cobalt species were found to be the most active. It has also been shown qualitatively that methanol dehydrogenation can be achieved using RuCl(OAc) supported on phosphine functionalised model- and poly-siloxanes.

CONTENTS

CHAPTER TWO : SYNTHESIS OF FUNCTIONALISED SILOXANES

CHAPTER THREE : IDENTIFICATION AND CHARACTERISATION OF FUNCTIONALISED ORGANOSILOXANES

CHAPTER FOUR : METAL COMPLEXED MODEL SILOXANES AND POLYSILOXANES

ABBREVIATIONS

acac	acetylacetonate (pentan-2,4-dionate)
AZBN	2,2'-azobis(2-methylpropionitrile)
bipy	2,2'-bipyridine
b.p.	boiling point
Bu	butyl
COD	cycloocta-1,5-diene
Cp	cyclopentadienyl
D	difunctional
DMF	dimethylformamide
D.P.	degree of polymerisation
D.V.B	divinylbenzene
en	ethylenediamine (1,2-diaminoethane)
G.C.	gas chromatography
G.P.C	gel permeation chromatography
hν	ultraviolet irradiation
I	spin isotope
INEPT	Insensitive Nuclei Enhancement Polarisation Transfer
IPA	isopropyl alcohol
L	ligand
M	monofunctional
Me	methyl
MeCN	acetonitrile
mm Hg	millimeters of mercury (pressure)
mmol	millimole
mol %	mole percentage of functional group in polymer
mvbipy	4-methyl-4'-4-vinyl-2,2'-bipyridyl
Mw	molecular weight
n/i	normal to iso ratio
nOe	nuclear Overhauser effect

OPTA	oligo-p-phenyleneterephthalimide
P	pressure
(P)	polymer support
PAA	poly(acrylic acid)
PAPMS	poly(aminopropylmethylsiloxane)
PCEMS	poly(cyanoethylmethylsiloxane)
Ph	phenyl
PVA	poly(vinyl alcohol)
py	pyridine
Q	tetrafunctional
R	alkyl group
RT	ambient temperature
SIL	silica
T	trifunctional
THF	tetrahydrofuran
TLC	thin layer chromatography
TFMSA	trifluoromethanesulphonic acid
UV	ultraviolet
VEP	vinyl endblocked polydimethylsiloxane
Vi	vinyl

Nuclear Magnetic Resonance (NMR):

d	doublet
dq	doublet of quartets
J	coupling constant (Hz)
m	multiplet
OFR	off frequency resonance
ppm	parts per million relative to TMS
q	quartet
s	singlet
t	triplet

δ	chemical shift
TMS	tetramethylsilane

Infrared (IR) Spectroscopy:

cm^{-1}	wavenumber
m	medium
s	strong
sh	shoulder
v	very
w	weak

CHAPTER ONE

INTRODUCTION

1.1. SUPPORTED CATALYSTS

1.1.1. INTRODUCTION

The preparation of supported catalysts formed by immobilizing active transition-metal complexes on solid supports such as organic polymers, inorganic oxides and related materials, has in the past decade become an area of intense research activity. This is reflected in many articles in books, review journals and papers[1-7]. These in turn are inspired by efforts to develop industrially competitive anchored catalysts which confer some of the benefits of homogeneous systems on heterogeneous catalysts of the type used so extensively on a large scale in the chemical industry.

1.1.2. PRINCIPLES AND BENEFITS OF HOMOGENEOUS CATALYSTS

The main principles and advantages of homogeneous catalysts can be summarised as follows:

a) Homogeneous catalysts are, by definition, dissolved in the reaction medium. Therefore, each of the catalyst metal atoms or ions has the potential to act as an active catalyst centre. In heterogeneous catalyst systems, only a proportion of the active sites are likely to be available to the reactants, and diffusion-controlled mass transfer and non-uniform reaction rates may result.

b) The high mobility of the homogeneous catalyst provides a higher probability of an active catalytic centre making an effective collision with the reactants than in the case of a heterogeneous catalyst. In addition, a reaction occurring at one active site is unlikely to reduce activity by obscuring another active site. Although homogeneous

catalysts will lose activity due to various processes such as decomposition and irreversible reactions with by-products, they do not suffer loss of activity by sintering as occurs on the surface of some heterogeneous catalysts. In addition, homogeneous catalysts normally operate under relatively mild conditions of temperature and pressure.

c) By variation of the metal, the oxidation state of the metal, the ligands coordinated to the metal, the reaction conditions, or the solvent used in the reaction, a great deal of control can be exercised over the selectivity of homogeneous catalysts, and hence higher yields of specific products can be obtained. The 'tailoring' of a catalyst can be controlled to such an extent that many chiral syntheses can be achieved on a moderate scale.[4,8]

d) Most importantly, homogeneous systems are amenable to mechanistic studies, so leading to the construction of improved and more active catalysts.

e) Homogeneous catalysts are also typified by high endurance, and can offer further economic advantages which include ease of scale-up, and a reduction in the number of steps used in the synthesis of a product.

Attempts to supplant heterogeneous catalysts have met with only limited success due to the separation problems associated with homogeneous systems, which can often only be accomplished with high energy expenditure, or with high product or catalyst loss. The

complete separation of the product from the reaction system is an obvious requirement and the process economics will be enhanced if effective separation can be achieved without affecting the performance of the catalyst. A number of separation procedures may be employed for homogeneous systems. These include simple distillation, solvent extraction or ion exchange techniques. In those cases in which the catalyst is part of a macromolecular system of high molecular weight relative to either the reactant or the product, then membrane filtration may be employed as an alternative to more usual procedures. In contrast to homogeneous catalysts, heterogeneous catalysts allow for ready separation of reaction products. Further to this, the catalyst systems may have good mechanical and often thermal stability which permits their use in packed and fluidised beds, and at elevated temperatures and pressures. The integrity of immobilised active transition-metal complexes is dependent on the stability of the support, and consequently, the use of a relatively active organic polymer for example, is a severe limitation in the possible applications of such materials.

1.1.3. TYPES OF SOLID CATALYST SUPPORT

The activity of supported catalysts often differs from that of the homogeneous catalyst, however, the ideal catalyst would be prepared by attaching a homogeneous catalyst to a support in such a way that the primary coordination sphere of the metal is essentially unchanged from that of the homogeneous system, and the attached complex is bathed by solvent and reactants. Thus, the resulting 'heterogenized-homogeneous' catalyst could function mechanistically as if it were in solution but it would operate as a separate immobile phase. The term

'heterogenized-homogeneous' is by no means applied exclusively, other terms including 'homogeneous-heterogeneous', 'hybrid-phase', 'polymer-anchored' and 'supported organometallic' catalysts have been widely used.

1.1.3. (a) ORGANIC SUPPORTS

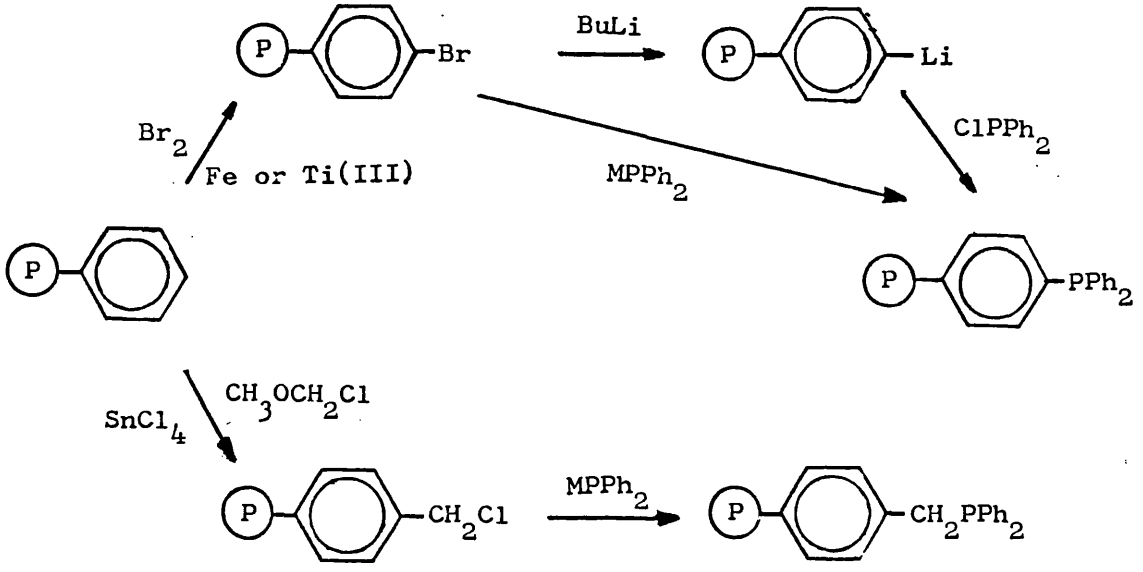
A wide range of organic supports are in use. Most commonly employed is polystyrene[1,4], alternatives include polybutadiene[9], polyvinylalcohol[10], polymethycrylate allyl chloride/divinylbenzene[11], polyphenylene-isophthalamide[12] and poly-4-vinylpyridine[13]. More recent examples include polybenzimidazole[14], polyallylamine[15] and cellulose[8]. Organometallic complexes which are catalytically active can be incorporated into organic polymers by several methods. The substituents of the polymer itself may act as ligands (as in polyamides, polyvinyl derivatives and occasionally polystyrene), or strong metal-binding species such as phosphines, amines or the cyclopentadienyl group can be introduced into the support.

(i) PREPARATION

Phosphorus donor ligands are commonly used to attach metal complexes to polymer supports and this example is taken to illustrate the two complementary approaches to catalyst preparation which can be employed. These involve either modification of a preformed polymer, or polymerisation of phosphine monomers. The former procedure has the advantage that the characteristics of the support (e.g. surface area, pore size, swelling properties) are already known and are not expected to be grossly altered on functionalisation.

Polystyrene is commonly used as a support because of its ready availability in several forms, its chemical inertness, and the ease with which ligands and metals may be anchored to it. Phosphine attachment to preformed polystyrene is commonly accomplished[9,16,17] using the routes illustrated in Scheme 1.

Scheme 1.



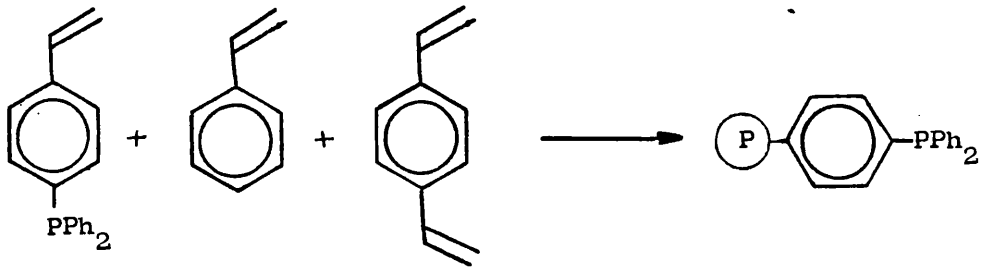
(M = Na or K)

Introduction of a p-chloromethyl group also provides an entry for the introduction of other ligands such as the isonitrile[18], cyclopentadienyl[19] and acetylacetonate[20] moieties.

Alternatively, phosphinated polymers can be prepared from phosphine containing monomers. Examples of such monomers include

vinyldiphenylphosphine, allyldiphenylphosphine and p-diphenylphosphinostyrene which are generally copolymerised with styrene or divinylbenzene[21-24]. The ligand loadings and cross-linking densities can be controlled to some degree by varying the amounts of monomers (Scheme 2).

Scheme 2

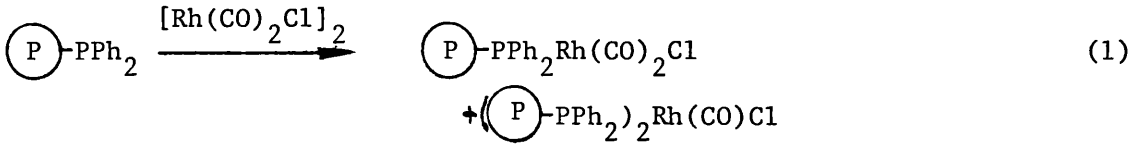


The use of polystyrene as a support matrix is, however, limited by the thermal and mechanical stabilities of the support, and reproducibility in functionalisation. Beads may fragment in stirred reactors and the upper thermal limit for most applications is 150 - 170°C. Although phosphine containing polymers based on polystyrene are still the most common catalyst supports, functionalised supports with cyclopentadienyl, amine and cyanide ligand endings are finding increasing importance.

(ii) IMMOBILISATION OF TRANSITION-METAL SPECIES ON ORGANIC SUPPORTS AND THEIR APPLICATIONS IN CATALYSIS

Diphenylphosphino-functionalised polystyrene resins have been widely investigated as supports for catalytically active complexes,[16,25-30]

and equations 1-5 illustrate several of the ligand replacement reactions used to prepare these materials. Commonly employed are carbonyl substitution, halide bridge-breaking, or ligand exchange reactions which may be effected by photochemical or thermal means.



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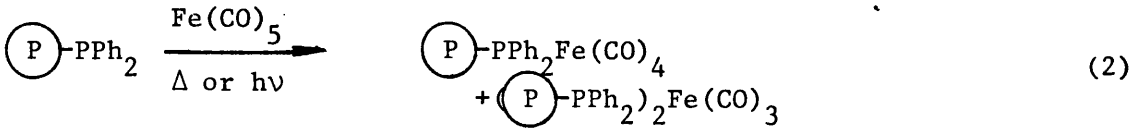

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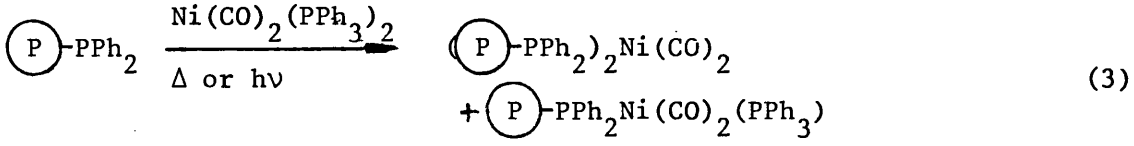

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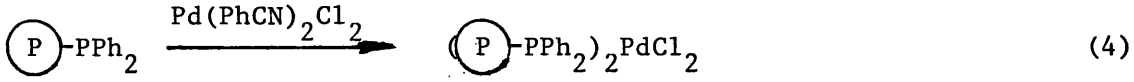

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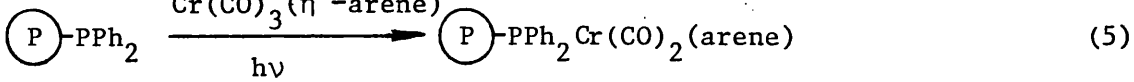


(5)

Pittman and co-workers have reacted $Co_2(CO)_8$ with a phosphinated polystyrene which can behave as a chelating support[16] (Scheme 3). The initial product was $[(P\text{-}PPh_2)_2Co(CO)_3]^+[Co(CO)_4]^-$ which was readily converted to the neutral material upon heating.

Scheme 3

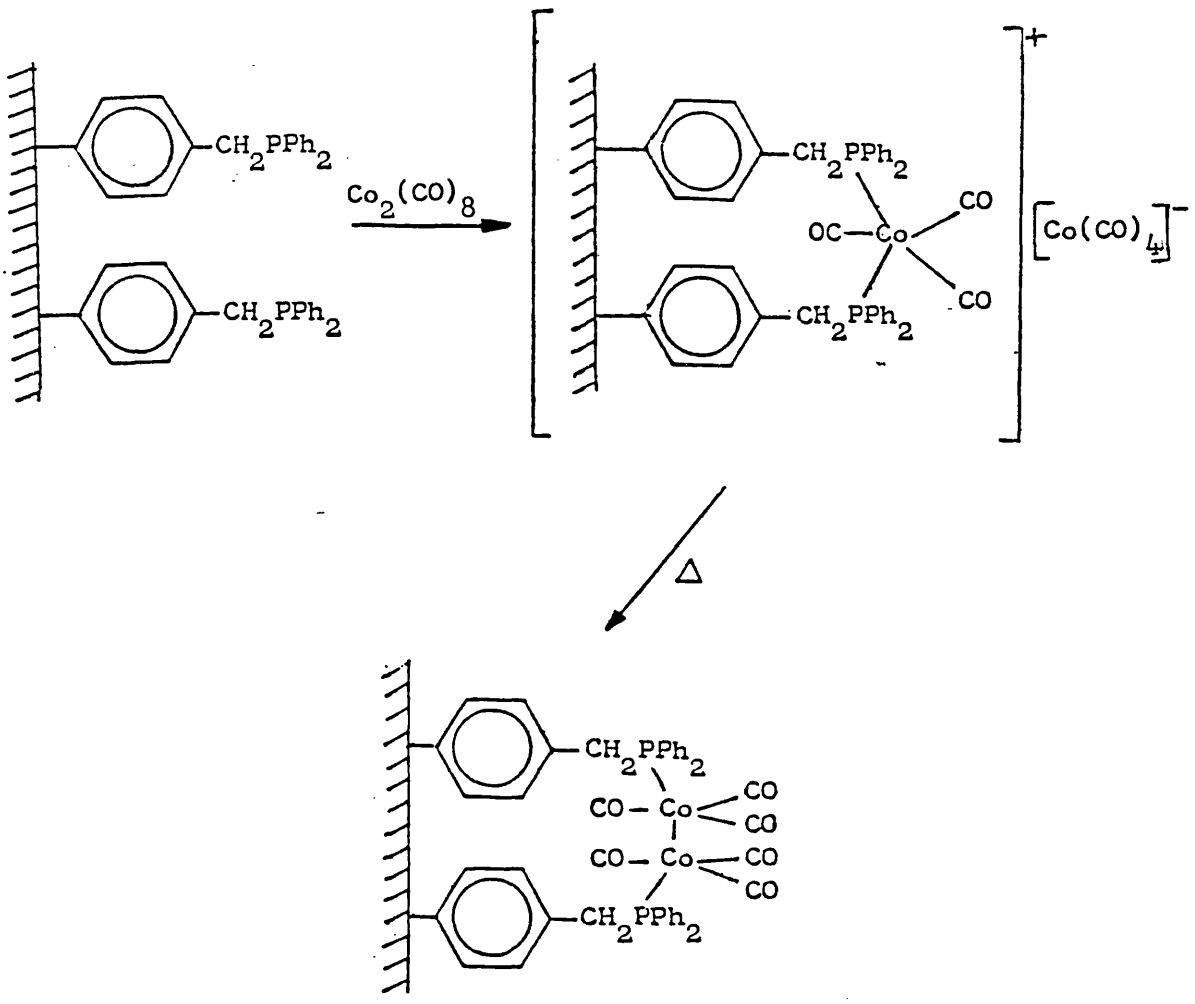
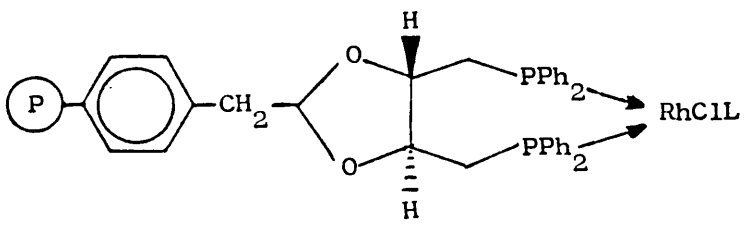


Table 1.1 summarises some of the applications of phosphinated polystyrene supported catalysts in various reactions of alkenes.

TABLE 1.1 EXAMPLES OF PHOSPHINATED POLYSTYRENE SUPPORTED CATALYSTS AND THEIR USE IN ALKENE REACTIONS

Metal Complex	Catalytic Action	Reference
$Co_2(CO)_8$	Hydroformylation	16
$Ni(CO)_2(PPh_3)_2$	Cyclooligomerisation	31
$PtCl_2$	Hydrogenation	32
$[Rh(CO)_2Cl]_2$	Carbonylation; Hydroformylation	33 34
$RhCl_3$	Hydrosilylation	35
$NiCl_2$	Polymerisation	36
$[RhCl(C_2H_4)_2]_2$	Hydrogenation	37
$CoCl_2$	Hydrogenation	4
$CoCl_2(PPh_3)_2$	Carbonylation; Hydroformylation	39
$RhCl_3$	Carbonylation Hydroformylation	38
$RhH(CO)(PPh_3)_2$	Carbonylation Hydroformylation	40

Many polymer immobilized asymmetric catalysts have also been described[4]. For instance the rhodium complex



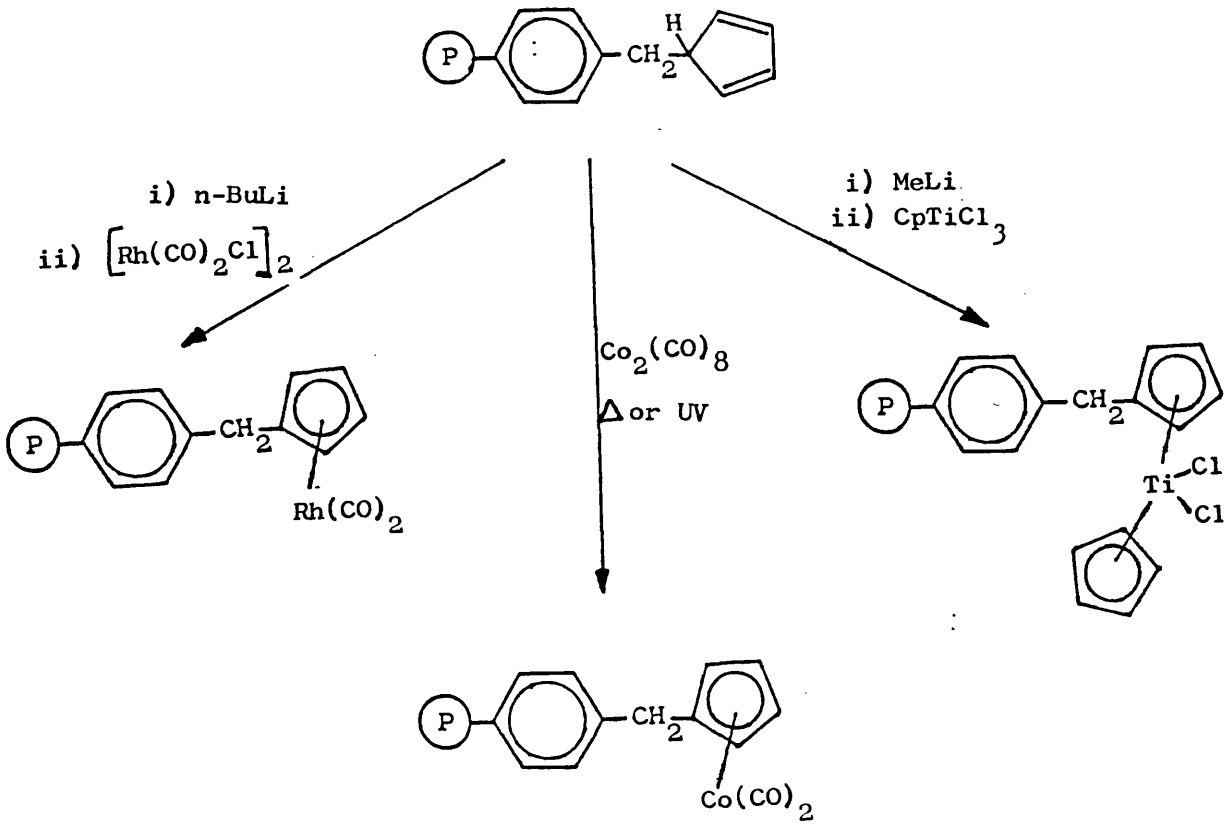
(I)

of 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)-

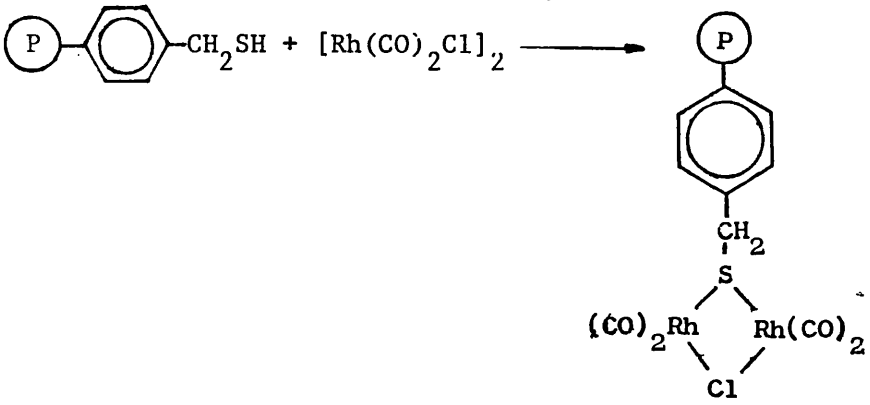
butane (diop) was immobilized on preformed styrene-2% DVB resins (I) and employed in the asymmetric hydrogenation of α-ethylstyrene and methyl atropate. It was also found to be a very efficient catalyst for the asymmetric hydrosilylation of ketones.

Cyclopentadienyl ligands have also been employed to attach a variety of rhodium[41], cobalt[41,42] and titanium[43] complexes as illustrated below (Scheme 4).

Scheme 4



Thiol[44] and amine[44,45] functionalised supports have been used in bridge-splitting reactions involving $[Rh(CO)_2Cl]_2$ (equations 6 and 7 respectively):



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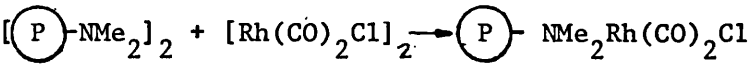
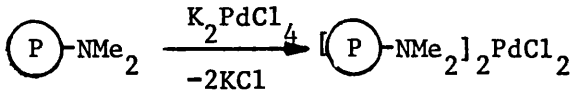


(7)

Dimethylaminated resins have also been used in metallation reactions involving platinum, palladium and rhodium chloride[46,47,48] (e.g. equation 8).



(8)

Examples of a selection of uses of polystyrene supported catalysts (excluding phosphine containing materials) are tabulated in Table 1.2.

TABLE 1.2 EXAMPLES OF POLYSTYRENE SUPPORTED METAL SPECIES AND THEIR CATALYSIS OF ALKENE REACTIONS

Functionality	Metal Complex	Catalytic Action	Reference
C_5H_5	$TiCl_3$	Hydrogenation	43
NR_2	$RhCl_3$,$PtCl_2$,$PdCl_2$	Hydrogenation	46,47,48
NR_2	$[RhCl(CO)_2]_2$	Hydroformylation; Carbonylation	49
NR_2	H_2PtCl_6	Hydrosilylation	50
SH	$[Rh(CO)_2Cl]_2$	Hydroformylation; Carbonylation	49
$-CO_2H$	$Ru(O_2CCF_3)_2(CO)(PPh_3)_2$	Dehydrogenation	51

Recently, examples of water or organic solvent soluble polymeric materials have been investigated as supports. Bayer et al[52] who incorporated metal species into a variety of linear, soluble poly(vinylpyrrolidinones) and poly(ethyleneimines), yielding active catalysts for ligand-directed regio- and stereo-selective hydrogenations. Table 1.3 illustrates some of these systems.

TABLE 13 CATALYST SYSTEMS FOR VARIOUS HYDROGENATIONS

POLYCHELATOGON	LOW MOLECULAR WEIGHT LIGAND	CENTRAL METAL ATOM	% METAL POLYMER
Poly(vinylpyrrolidinone)	-	Rh	5
	-	Pd or Pt	1
	Alanine	Pd	0.5
Poly(ethyleneimine)	-	Pd	1
	Benzonitrile	Pd	1
	Alanine	Ni	2

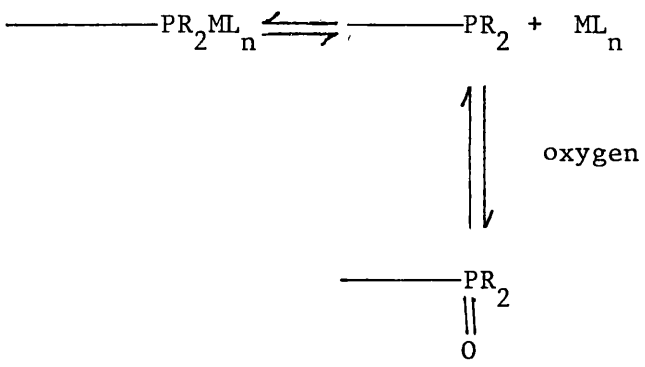
Yokoi et al[53,54] have examined the interaction between cupric ions and polyvinyl alcohol (PVA) and poly(acrylic acid) (PAA) in aqueous solutions. When the cupric ions were solubilized by PVA at pH>6, the ions exist as the olated polynuclear complex of $Cu(OH)_2$ and at pH<6 as ordinary hydrated ions. The authors attributed this solubilization mechanism to inclusion in which $Cu(OH)_2$ is included by the hydrophobic backbone of PVA chains with hydrophilic OH groups directed towards the aqueous phase. Similar interactions were observed with PAA. The authors did not comment on any catalytic or other applications of these systems.

Ennis et al[55] have successfully prepared water soluble copolymers containing $[Ru(bipy)_3]^{2+}$ centres by the copolymerisation of $[Ru(bipy)_2(mvbipy)]^{2+}$ (mvbipy = 4-methyl-4'-4-vinyl-2,2'-bipyridyl) and 4-vinylpyridine, followed by quaternisation of the vinylpyridine groups with ethyl bromide. The photophysical properties of the metallated copolymers were very similar to those found for $[Ru(bipy)_3]^{2+}$, though yields in the reduction of methylviologen in the presence of $N(CH_2CH_2OH)_3$ were found to be lower than for aqueous $[Ru(bipy)_3]^{2+}$.

All these examples centre on mononuclear metal species, but reflecting current interest in metal aggregatives, Hirai et al[56] have reported the immobilization of colloidal platinum particles onto a polyacrylamide gel containing aminoethyl groups. The resulting catalysts exhibited high activities in the hydrogenations of olefins at 30°C under 1 atmosphere pressure. In just a few instances, O-ligated mononuclear complexes of transition-metals, e.g. (P)-acacRh(CO)$_2$, have been used in catalytic hydrogenations[57], and some binary metal carbonyl clusters supported on phosphine-functionalised polystyrene are also known to produce hydrogenation catalysts[58-61].

The long term use of polymer-supported catalysts, particularly in continuous, fixed-bed processes leads to the major problem of loss or leaching of the metal from the catalyst.[4,62,63,64]. If the ligands linking the metal to the polymer are involved in dissociation equilibria with the free metal entity under catalytic conditions, leaching can be serious, particularly if the free ligand or released metal species subsequently reacts irreversibly with impurities, products or reactants present in the reaction media.

e.g.



The extent of metal loss may be reduced by

(i) increasing the ligand:metal ratio in the polymer;

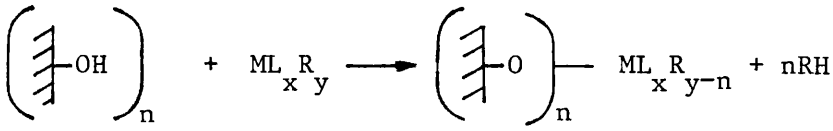
(ii) avoiding the use of coordinating solvents;

(iii) using microporous resins which are functionalized with ligand throughout, instead of surface functionalized macroreticular beads;

(iv) using chelating ligands.

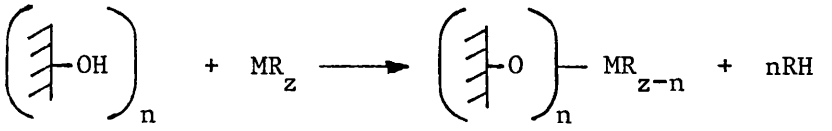
1.1.3. (b) INORGANIC SUPPORTS

Inorganic oxides, especially silica, alumina, zeolites and other minerals are commonly used as supports[65,66,67]. Such supports possess active surface groups which may be used directly for immobilizing transition-metal species. Thus the interaction of organometallic compounds ML_xR_y or MR_2 (M = transition element, R = organic ligand, L = anion or other inorganic ligand) with surface hydroxyl groups of the support may lead to immobilization via the following reactions (equations 9 - 11).



(9)

or



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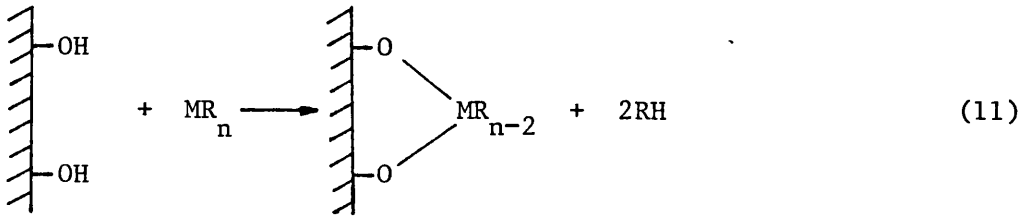
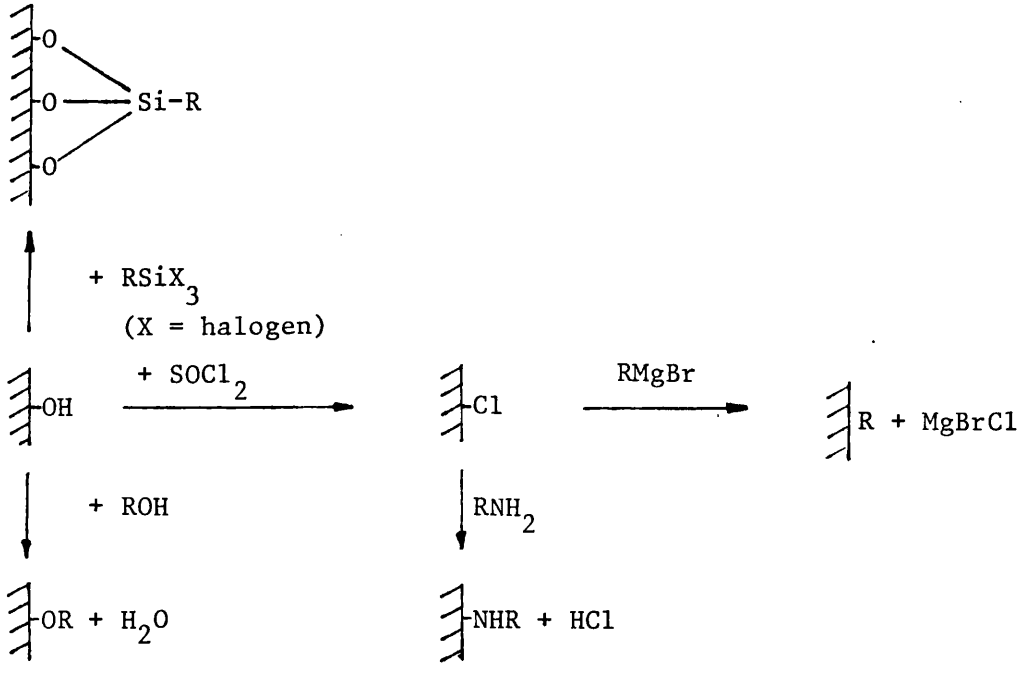


(11)

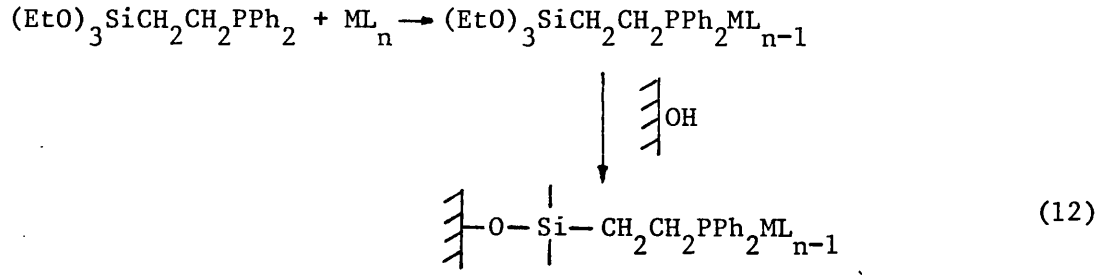
The product resulting from such an interaction can then be used directly as a heterogeneous catalyst.

Alternatively the surface may be functionalized by reaction with a reactive chloro-compound as illustrated in Scheme 5[68,69],

Scheme 5 (R = alkyl)



or by reaction with a bifunctional silicon compound which may then be metallated (equation 12), or derivatised further prior to metallation (equation 13).



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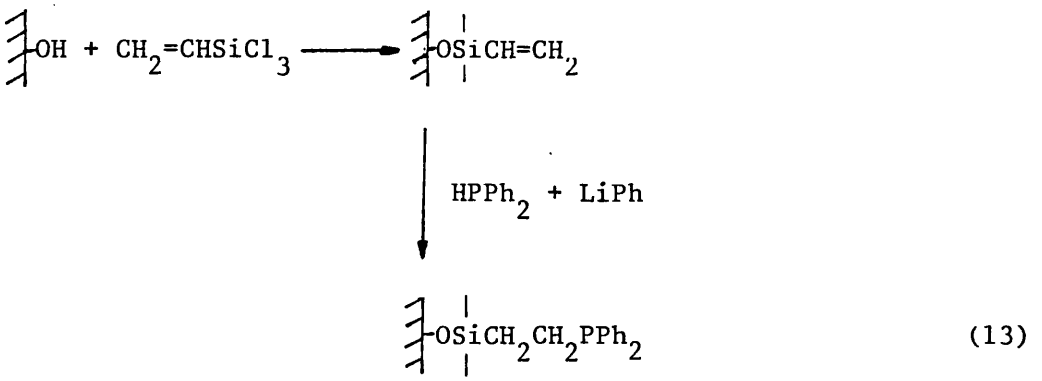


(13)

Analogous procedures have been used to produce -CN, $-NMe_2$ and -py functionalised silica whose metallated derivatives have been used to catalyse a range of organic reactions, some of which are summarised in Table 1.4.

In the many papers published on metal oxide supported catalysts, few authors have noted unusual problems in their use. However, Goldstein et al[74] recently reported anomalous results on using silica or alumina functionalised with $(C_2H_5O)_3Si(CH_2)_nX$ (where X is a donor group capable of coordinating to metal centres) as

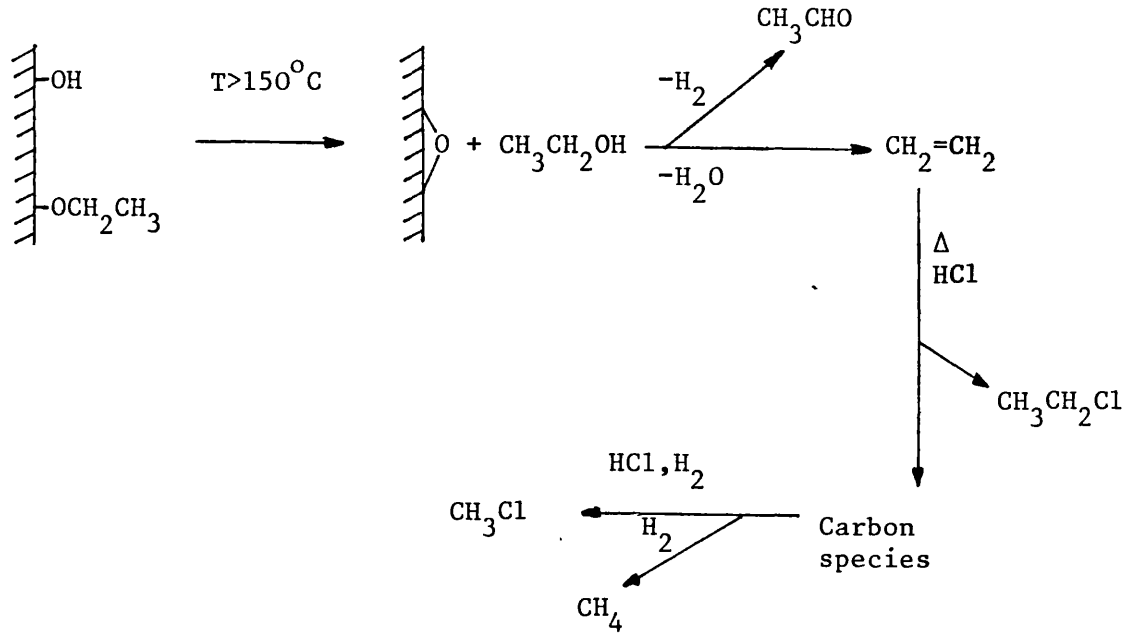
TABLE 1.4 EXAMPLES OF SILICA SUPPORTED CATALYSTS AND THEIR CATALYSIS OF ALKENE REACTIONS

Functionality	Metal Complex	Catalytic Action	Reference
PPh_2	Na_2PdCl_4	Hydrosilylation	70
PPh_2, NMe_2, CN, C_5H_4N	$PdCl_2$, $RhCl_3$ or H_2PtCl_6	Hydrosilylation	70
CN	$[Rh(CO)_2Cl]_2$	Hydroformylation	71
PPh_2	$[RhCl(C_2H_4)_2]_2$	Hydrogenation	72
PPh_2	$Ni(COD)_2$	Polymerisation	73
PPh_2	$[Co(acac)_2]$	Hydroformylation	74

supports for iridium clusters. On reaction with a gaseous mixture of H_2/CO/HCl, products were detected which result from reaction with organic residues introduced onto the solid surface during functionalisation of the oxide. Scheme 6 shows the author's postulated mechanism for the decomposition of the ethoxy groups, which originate from the silylating agent, and yield methyl chloride in subsequent reaction with H_2/CO/HCl

mixtures. The generality of these results for other metal oxide silylation reactions remains to be determined.

Scheme 6*



* Phosphinated ligand groups omitted for clarity

1.1.3. (c) OTHER ORGANOELEMENTAL POLYMERS

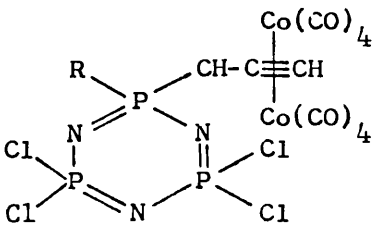
Recently considerable interest has centred on many other polymeric compounds with a predominantly inorganic backbone. Macromolecules with a homochain based on boron, silicon, phosphorus and sulphur are known, but carbon is distinguished amongst these elements by the high energy of the bond between its atoms, being superior in this respect to all other elements (Table 1.5).[75]

Table 1.5

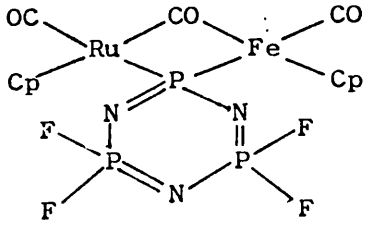
Bond	Bond energy in homochain polymer ($kJmol^{-1}$)	Bond	Bond energy in heterochain polymer ($kJmol^{-1}$)
		B-O	499.2
C-C	334.7	C-O	330.5
Si-Si	205.0	Si-O	373.6
P-P	221.8	P-O	341.8
S-S	263.6	C-N	276.1

A completely different picture emerges in the case of heterochain polymers where C-O and C-N bond energies are not particularly high, as is seen in Table 1.5. Thus heterochain polymers, particularly those based on Si and P are stable and have been metallated and in several instances used as catalyst supports. For example, cyclophosphazenes containing transition metals have been investigated particularly at Pennsylvania State University[76,77,78]. These materials are readily formed by reaction between organometallic reagents and cyclophosphazenes, and are prototypes for linear polymer analogues.

e.g.



(II)



(III)

The same group of workers have examined more recently a cobalt hydroformylation catalyst prepared from $Co_2(CO)_8$ supported on phosphinated polyphosphazenes[79] (IV) and (V). The catalyst was

$$[NP(OPh)_{1.7}(OC_6H_4PPh_2)_{0.3}]_n \qquad \text{(IV)}$$

$$N_3P_3(OPh)_5(OC_6H_4PPh_2) \qquad \text{(V)}$$

initially active, but revealed a time-dependent decrease in catalytic activity due to a cobalt-mediated phosphorus-carbon bond cleavage. The authors in previous work[80,81] have noted similar catalyst deactivation with organic polymer-immobilized catalyst systems.

1.1.4. POLYSILOXANE SUPPORTS

Most current research on supported catalysts has focused primarily on solid inorganic and organic supports[1,3] with relatively few studies being carried out on soluble polymer catalysts. Even fewer have focused attention on solventless fluid polymer systems because of the paucity of such materials. The best known, and most promising systems involve polysiloxanes, which in a few isolated papers have been shown to be able to support transition-metal catalysts, although neither the detailed structure of the polymer backbone nor the constitution of the catalytically active sites in the polymer matrix have been well-defined in the majority of these studies.

Interest in metal-complexed phenylsiloxane polymers originally centred on a comparison of these materials with the corresponding polystyrene-supported complexes. Brown[82] first reported the exceptional chemical, mechanical, and thermal stability for soluble

'ladder' polyphenylsiloxanes in 1963, but it was not until 1975 that reports of metal carbonyl entities bonded to the aryl rings of similar siloxanes appeared.

There are two general routes used to prepare polysiloxane-supported transition-metal catalysts, and these are exemplified below.

(i) Hydrolysis of $Cl_n Si(R)_m$-L Species (n = 3,2,1; m = 0,1 or 2)

In view of the popularity of phosphine substituents in functionalised organic polymers and insoluble inorganic supports, it is not surprising to find that much of the early work on siloxanes centred on phosphinated organosilicon polymers and their metallated derivatives. About ten years ago Brzezinska and Cullen[83] prepared a range of soluble (chlorosilyl)phosphine and siloxyphosphine complexes of rhodium(I) in high yields via the uv-induced reaction of diphenyl-phosphines with vinyl- and octenyl-alkyl and halo-silanes (equation 14)

$$R'(R'')_2Si(CH_2)_nCH=CH_2 + HPPh_2 \longrightarrow R'(R'')_2Si(CH_2)_{n+2}PPh_2 \qquad (14)$$

n = 0, R' = R'' = Me

n = 0, R' = Me, R'' = Cl

n = 0, R' = Me, R'' = $OSiMe_3$

n = 0, R' = R'' = Cl

n = 6, R' = R'' = Cl

The same authors[84,85] also prepared polymeric siloxyphosphine-rhodium(I) complexes of the phosphines $Cl_3Si(CH_2)_nP(C_6H_5)_2$ (n = 2,8) by hydrolysis either alone or in the presence of excess ligand or Cl_3SiCH_3, to afford insoluble polymeric globules. Although these

metal-doped polymers possessed catalytic activity for the hydrogenation of alkenes, they were poorly characterised and non-reproducible.

$$[Cl_3Si(CH_2)_nP(C_6H_5)_2]_3RhCl + mCH_3SiCl_3 \xrightarrow{H_2O}$$

$$[O_{3/2}Si(CH_2)_nPPh_2]_3RhCl(O_{3/2}Si(CH_3)_3)_m$$

(n = 2,8; m = 0-200) (15)

$$[Cl_3Si(CH_2)_2P(C_6H_5)_2]_4Rh_2Cl_2 + mCH_3SiCl_3 \longrightarrow$$

$$[O_{3/2}Si(CH_2)_2P(C_6H_5)_2]_4Rh_2Cl_2(O_{3/2}Si(CH_3)_3)_m$$

(m = 0-200) (16)

$$[Cl_3Si(CH_2)_2P(C_6H_5)_2]_3RhCl + mCl_3Si(CH_2)_2P(C_6H_5)_2 \xrightarrow{H_2O}$$

$$[O_{3/2}Si(CH_2)_2P(C_6H_5)_2]_3RhCl(O_{3/2}Si(CH_2)_2P(C_6H_5)_2)_m$$

(m = 0.7) (17)

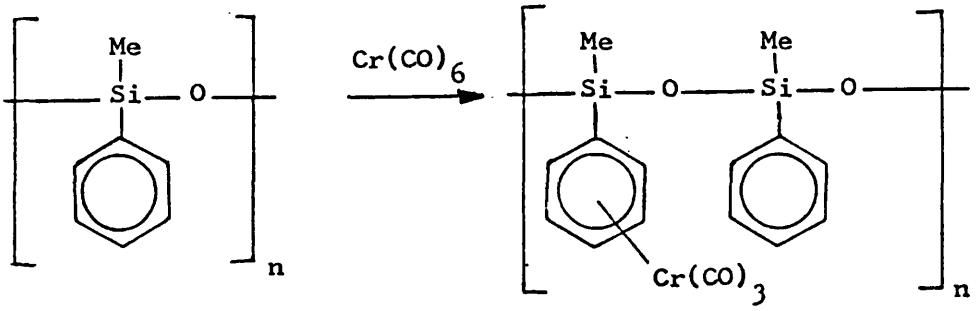
Farrel *et al*[86] produced polymer attached chlorocarbonylrhodium(I) complexes by metallating with $RhCl(CO)(PPh_3)_2$ (equation 18) a series of poly(organomethylsiloxanes) containing diphenylphosphine groups. These materials are soluble in a wide variety of organic solvents.

$$\underline{trans}\text{-}RhCl(CO)(PPh_3)_2 + 2(\text{P})\text{-}PPh_2)$$

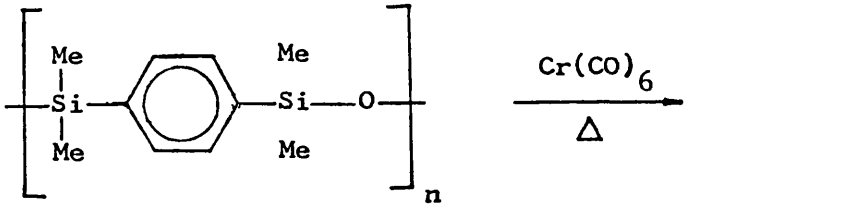
$$\xrightarrow{\text{benzene}} \underline{trans}\text{-}RhCl(CO)(\text{P})\text{-}PPh_2)_2 + 2PPh_3 \quad (18)$$

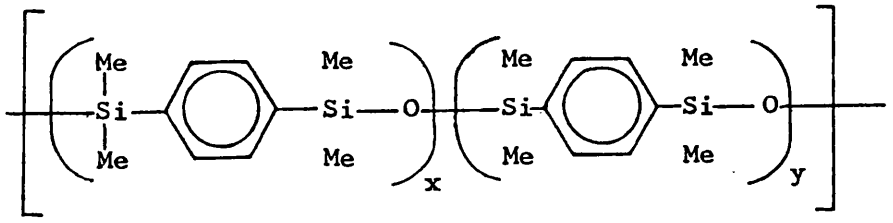
(ii) Direct Metallation of the Polymer

The other main route used for the preparation of polysiloxane-supported catalysts involves the addition of metal species directly to the polymer or to its modified form. Thus Pittman et al[87] who had previously prepared tricarbonylchromium complexed polystyrene by the direct reaction of the polymer with chromium hexacarbonyl, extended their studies to include the metallation of polysiloxanes (equations 19 and 20) with up to 19.3% metallation[88]. Awl et al[89]



(19)



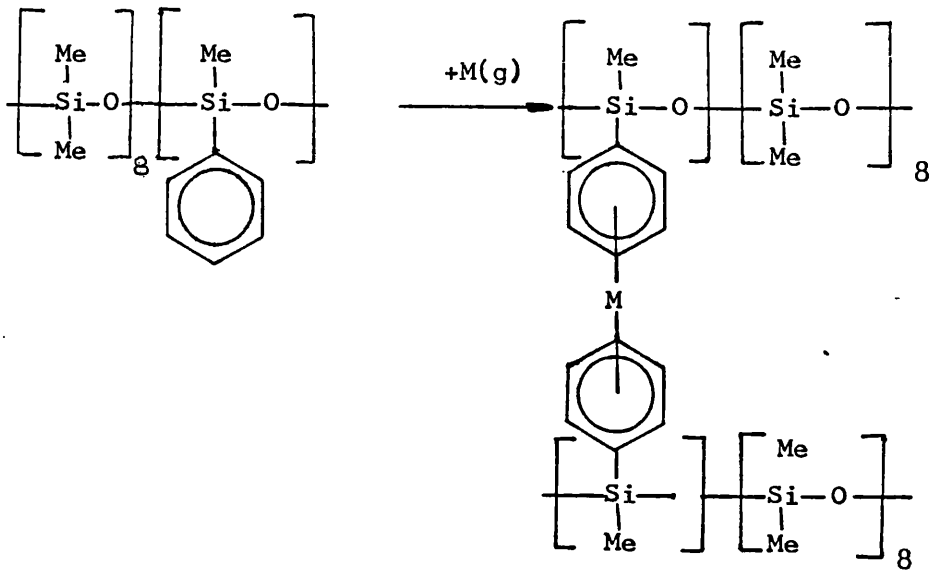


(20)

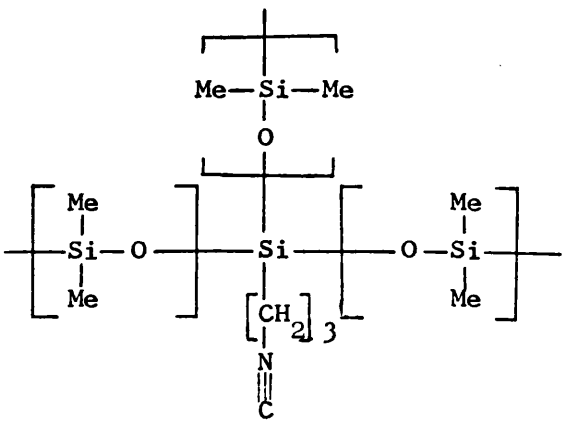
prepared soluble tricarbonylchromium complexes by reacting chromium hexacarbonyl with a ladder polyphenylsilsesquioxane and with a linear polydiphenylsiloxane. These silicone polymer complexes catalysed the stereoselective hydrogenation of methyl sorbate to cis-3-hexenoate in cyclohexane and THF and could be recovered from THF for reuse by precipitation-filtration. Loss of catalytic activity associated with loss of $Cr(CO)_3$ was, however, observed on recycling. These results support a mechanism that involves initial dissociation of $Cr(CO)_3$, a significant portion of which does not reassociate with the polymer phenyl groups. Supported trimetallic catalysts prepared by salt impregnation techniques have been shown to exhibit advantages over their respective bimetallic counterparts[90,91] which include enhanced stability towards segregation, sintering, and poisoning in hydrocarbon reforming processes. Francis et al have reported that "organotrimetal polymers" containing three different mononuclear metal sites can be readily generated by the metal vapour-fluid matrix technique[92-93]. Poly(methylphenylsiloxane) was originally shown to react with the metal vapours of Ti, V, Cr, Mo and W (in a metal vapour rotary reactor) to give a liquid bis(arene)-organometallic polymer[94], as shown in Scheme 7.

Further work extended this approach to organometallic polymers containing mononuclear and cluster metal sites randomly distributed throughout the polymeric structure, but no synthetic uses of these materials were reported. More recently, Francis et al[95] have carried out matrix-scale metal vapour reaction of iron and nickel

Scheme 7.



with the isocyano-functionalised polysiloxane (VIII) to afford novel polymer-encapsulated mononuclear metal isocyanide complexes

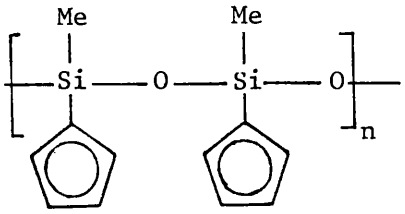


(VIII)

[$M(CNR)_n$; M = Fe, n = 5; M = Ni, n = 4]. The iron complex was then photolysed to yield the polymer attached binuclear $Fe_2(CNR)_9$ species, while cobalt vapour yields a binuclear species directly.

There have been relatively few papers describing water soluble polyorganosiloxanes[96], and even fewer relate to water-soluble polyorganosiloxane-metal complexes. However, Koyama et al[97] showed recently that the water solubilities of polyorganosiloxanes containing amine functionalities are pH dependent. The authors anticipate that copper(II) derivatives of these siloxanes will show catalytic activity.

Wang et al[98] have shown that a platinum complex of poly-γ-amino-propylsiloxane when used as a supported liquid phase catalyst is active for the hydrosilylation of olefins and can be reused several times. They also investigated[99] the preparation and reactions of a supported poly-γ-mercaptopropylsiloxane-platinum complex which was found to catalyse the addition of triethoxysilane to 1-hexene in over 90% yield at ambient or elevated temperatures. This material could be recycled many times without any appreciable loss in catalytic activity. Curtis et al[100] have prepared titanocene anchored derivatives of tetramethyldisiloxane and poly(methylsiloxane). The latter species can be considered as an analogue of organic polymer and silica supported titanocene derivatives prepared by other workers[101,102]. Chlorination of poly(methylsiloxane) followed by reaction with sodium cyclopentadienide yields the poly(cyclopentadienyl-methylsiloxane)(IX) which on reaction with sodium metal or n-butyllithium affords the anionic cyclopentadienide derivative, which in turn reacts with $TiCl_4.2.py$ to yield $[1,1'\text{-}\eta^5,\eta^5\text{-}(Me_2Si_2O_2)(C_5H_4)_2TiCl_2]_n$.



(IX)

In a series of papers[103-6] Harrod et al have explored the synthesis and fundamental properties of some substituted cyclosiloxanes as frameworks for sterically controlled, multifunctional catalyst systems. The compounds $[-Si(CH_3)(R)O-]_n$ ($R = Co(CO)_4$, n = 4 and 5; $R = CpFe(CO)_2$, n = 4) were prepared by reactions of the appropriate compounds (R = H) with $Co_2(CO)_8$ and $[CpFe(CO)_2]_2$ respectively[104]. The authors in a later publication[106] prepared and characterised cyclosiloxanes $[-Si(CH_3)(R)O-]_n$ ($R = PhCr(CO)_3$, n = 3, cis, cis, cis and cis, trans, trans; n = 4, cis, trans, cis, trans and a mixture of all possible isomers), complexes being obtained in an isomerically pure state by employing conventional synthetic procedures. (The use of ^{1}H-nmr spectroscopy to determine the isomeric compositions of cyclosiloxanes is described in Chapter 3). The ability of $[-SiMe\{Cr(CO)_3\}O-]_3$ to catalyse the hydrosilylation of 1,3-pentadiene by triethoxysilane was compared to those of [(trimethoxysilyl)benzene]-, [(trimethylsilyl)benzene]-, and (benzene)chromium-tricarbonyls[106]. These systems are more commonly used as catalysts for the hydrogenation of dienes[107] and relatively little literature is available on their activity as hydrosilylation catalysts[108]. However, the authors observed that neither the activities nor the specificities of this series of catalysts vary to any significant degree, which supports the initial mechanistic step proposed by Cais[107] for the analogous hydrogenation reaction, in which displacement of the tricarbonylchromium moiety from the arene occurs.

Under certain conditions, polymer degradation may become a major problem in using polysiloxane derivatives as supports for transition-

metal catalysed reactions. For instance, reactive halogen-containing metal reagents may cleave the Si-O chains and hence cause depolymerisation with concomitant alteration of the catalysts activity. Alternatively, reactions leading to organic radical formation are likely to be deleterious to the integrity of the polymer. Provided such reactions are avoided polysiloxanes provide interesting alternative support systems whose usefulness remains to be exploited.

As indicated earlier, in many of these studies the nature and structure of the polymeric siloxane framework, and often the immediate metal coordination sphere, have been largely disregarded in favour of the catalytic processes which can be achieved. In the following section factors affecting the formation and structure of the polymer matrix are considered.

1.2. SILOXANES

1.2.1. INTRODUCTION

Polyorganosilcxanes or silicone polymers are as a generic type intermediate in composition between the purely inorganic silicates and the organic polymers used so widely in the plastics industry. They are the only class of semi-inorganic polymers to date, which have achieved great commercial importance and their properties reflect their hybrid composition in many respects. The silicon atoms in polyorganosiloxanes can be chemically linked to one, two or three organic groups, the remaining valencies being satisfied by oxygen. The symbols M, D, T and Q have been introduced to represent

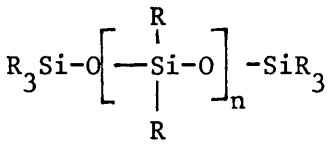
the mono-, di-, tri- and tetrafunctional siloxane units respectively (Table 1.6). The complex ion $[SiO_4]^{4-}$ is the structural unit from which the three-dimensional lattices of the modifications of silica and the silicates are formed.

Table 1.6 STRUCTURAL UNITS OF POLYORGANOSILOXANES

Structural formula	Composition	Functionality	Symbol
$R_3Si\text{-}O\text{-}$	$R_3SiO_{1/2}$	monofunctional	M
$-O-\overset{\overset{R}{\vert}}{\underset{\underset{R}{\vert}}{Si}}-O-$	$R_2SiO_{2/2}$	difunctional	D
$-O-\overset{\overset{R}{\vert}}{\underset{\underset{O}{\vert}}{Si}}-O-$	$RSiO_{3/2}$	trifunctional	T
$-O-\overset{\overset{O}{\vert}}{\underset{\underset{O}{\vert}}{Si}}-O-$	$SiO_{4/2}$	tetrafunctional	Q

Polyorganosiloxanes show a great diversity in their properties and this is primarily a result of the flexible Si-O-Si linkage, the degree of cross-linking, the molecular weight of the material, and the incorporation of fillers.

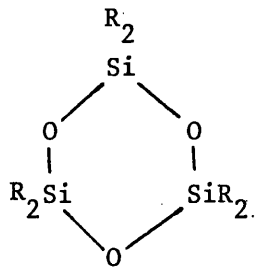
i) Most relevant to our studies is the combination of mono- and difunctional siloxane units leading to linear siloxanes of various chain lengths.



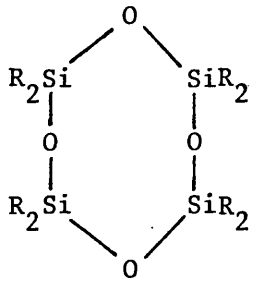
(X) $[M_2D_n]$

ii) The monofunction siloxane unit can also combine with itself only once to give a hexaorganodisiloxane $R_3SiOSiR_3$ of the type M_2,

iii) The difunctional units can also form closed rings of various sizes,



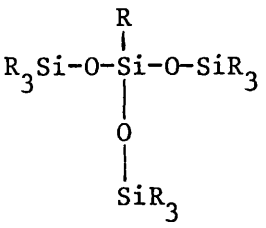
(XI) $[D_3]$



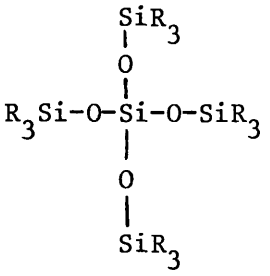
(XII) $[D_4]$

iv) Combinations of trifunctional siloxane units generally gives molecules cross-linked randomly in three dimensions

v) The combination of mono- and tri- or tetrafunctional siloxane units leads to low molecular weight structures such as (XIII) and (XIV).

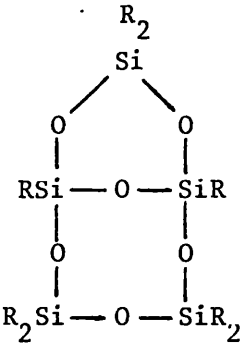


(XIII) $[M_3T]$



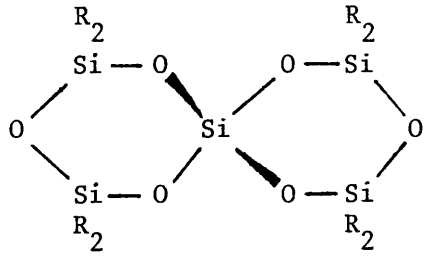
(XIV) $[M_4Q]$

vi) Di- and trifunctional siloxane units can yield macromolecules which have the nature of networks when the content of T units is high, i.e. $D_n T_m$ (m>n). An excess of D units gives chains which are cross-linked or branched at long intervals. D and T units can also combine to yield products of low molecular weight as in (XV) below.



(XV) $[D_3T_2]$

vii) The combination of di- and tetrafunctional units can lead to three dimensional highly cross-linked molecular structures as for di- and trifunctional units. In addition, under certain conditions, spiro compounds may result. The basic structural unit is determined by the tetrahedral arrangement of the oxygen atoms around the silicon atom in the Q unit, e.g.



(XVI) $[D_4Q]$

1.2.2. SYNTHETIC PROCEDURES

The usual method[109,110] for producing polyorganosiloxanes involves three general stages:

a) Preparation of chlorosilanes.

b) Hydrolysis of chlorosilanes to yield siloxane intermediates.

c) Polymerization of siloxane intermediates.

a) Preparation of Chlorosilanes

The major reaction used in the silicone industry for making methylchlorosilanes was discovered in 1941 by Rochow and is known as the method of 'direct synthesis'. Methyl chloride reacts with a stirred or fluidized bed of powdered silicon containing copper powder as catalyst at ca. 570K (equation 21).

$$CH_3Cl(g) + Si(s) \xrightarrow[Cu]{570K} (CH_3)_2SiCl_2(g) + CH_3SiCl_3(g) + (CH_3)_3SiCl(g) \qquad (21)$$

The reaction is exothermic and conditions are usually adjusted to give optimum yields (>80%) of dimethyldichlorosilane, which is separated from the other products by fractional distillation. Phenyl chlorosilanes

are also made by the direct reaction of benzene with trichlorosilane, or by the reaction of chlorobenzene, magnesium and a chlorosilane, which involves a Grignard intermediate. Vinyl chlorosilanes are made either by the platinum catalysed addition of acetylene to chlorosilanes or by reaction of the latter with vinyl chloride in a hot tube (equations 22 - 24).

$$CH{\equiv}CH(g) + HSiCl_3(l) \xrightarrow{Pt} CH_2{=}CH\text{-}SiCl_3(l) \quad (22)$$

$$CH{\equiv}CH(g) + (CH_3)_2SiHCl(l) \xrightarrow{Pt} CH_2{=}CH\text{-}Si(CH_3)_2Cl(l) \quad (23)$$

$$CH_3SiHCl_2(g) + CH_2{=}CHCl(g) \xrightarrow{Pt} CH_2{=}CH\text{-}Si(CH_3)Cl_2(g) \quad (24)$$

Many other organofunctional chlorosilanes are also made by Si-H addition reactions to substituted alkenes (equation 25).

$$CH_3OCOC(CH_3){=}CH_2(l) + HSiCl_3(l) \xrightarrow{Pt} CH_3OCOC(CH_3)CH_2CH_2SiCl_3(l) \quad (25)$$

b) Hydrolysis of Chlorosilanes

Hydrolysis of the various organofunctional silanes normally leads to silanols. Sterically hindered monomers can be isolated and characterised, and X-ray structure determinations have been carried out on representative examples such as dicyclohexylsilanediol[111]. However, the majority spontaneously condense by elimination of water at ambient temperature to yield various polymeric siloxanes. The M,D,T and Q siloxane units are obtained from the functional silanes as indicated in Table 1.7.

TABLE 1.7 HYDROLYSIS PRODUCTS OF M,D,T AND Q SILOXANE UNITS

Silane[a]	Generally Unstable Intermediate	Siloxane Unit
R_3SiX	$R_3Si(OH)$	$R_3SiO_{1/2}$
R_2SiX_2	$R_2Si(OH)_2$	$R_2SiO_{2/2}$
$RSiX_3$	$RSi(OH)_3$	$RSiO_{3/2}$
SiX_4	$Si(OH)_4$	$SiO_{4/2}$

[a] X = Halogen

The rate of hydrolysis increases with the polarity of the Si-X bond and with the number of halogen atoms attached to each silicon

$$\equiv SiF < \equiv SiCl < \equiv SiBr < \equiv SiI$$

$$SiCl_4 > RSiCl_3 > R_2SiCl_2 > R_3SiCl$$

atom, and it is also affected by the type and number of organic groups. Substituents of large steric bulk hinder attack by water molecules, and highly electronegative groups strengthen the Si-X bond and hence lower the reactivity of the halosilane towards water. These factors are very important industrially in the choice of methods for the formation of copolymers. If the different components of a chlorosilane mixture have a different ease of hydrolysis and self-condensation, it may prove difficult to achieve a copolymer using this method.

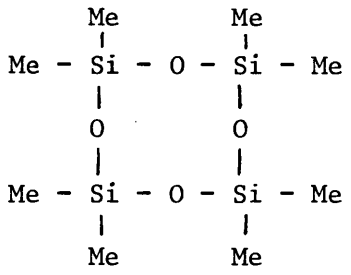
The commercially most important dialkyldihalosilane $(CH_3)_2SiCl_2$ is converted on hydrolysis into dimethyl silanediol, $(CH_3)_2Si(OH)_2$, which condenses spontaneously at room temperature to a mixture of cyclic

and linear siloxanes (equation 26), the major component being

$$(CH_3)_2SiCl_2(l) + H_2O(l) \longrightarrow [(CH_3)_2SiO]_m(l) + HO[Si(CH_3)_2O]_nH(l) + HCl(g) \quad (26)$$

(m, n = 3-15)

octamethylcyclotetrasiloxane (XVII)



(XVII)

The hydrolysate, $HO[Si(CH_3)_2O]_nH$, can be converted to cyclic siloxanes, which are distilled off as they are formed, by heating with potassium hydroxide, which catalyses the rearrangement and condensation process. Methyldichlorosilane can be hydrolysed in a similar way (equation 27).

$$CH_3SiHCl_2(l) + H_2O(l) \longrightarrow (CH_3SiHO)_m(l) + HO[SiH(CH_3)O]_nH(l) + HCl(g) \quad (27)$$

However, Si-H containing siloxanes cannot be subjected to alkali catalysed rearrangement reactions due to the sensitivity of the SiH groups to hydrolysis under those conditions. Disiloxanes which provide monofunctional end-groups in the ring-opening polymerisation of cyclic siloxanes are produced by hydrolysis of trimethyl chlorosilane (equation 28) and dimethyl chlorosilane respectively (equation 29).

$$2(CH_3)_3SiCl(l) + H_2O \longrightarrow (CH_3)_3SiOSi(CH_3)_3(l) + 2HCl(g) \quad (28)$$

$$2(CH_3)_2SiHCl(l) + H_2O(l) \longrightarrow (CH_3)_2HSiOSiH(CH_3)_2(l) + 2HCl(g) \quad (29)$$

c) Polymerisation of Siloxane Intermediates

In the production of silicones the process known as 'equilibration', whereby Si-O linkages of a siloxane or mixture of siloxanes are continuously broken and reformed until the system reaches equilibrium at the thermodynamically most stable state, is of considerable importance. The reaction has the effect of converting a mixture of siloxanes whose molecular weight distribution curve has a number of maxima into one having a single maximum. Although heating alone will bring about this process, acids or bases are commonly used as catalysts.

Molecular weight control of polysiloxanes is achieved by the use of "endblockers", which introduce a non-reactive group such as $-OSiMe_3$ (equation 30). Polymers are also frequently endblocked with reactive groups such as Cl, OR and OAc (equation 31), if they are required for further synthetic elaboration.

$$YOY + nD_4 \longrightarrow YO(Me_2SiO)_{4n}Y \quad (30)$$

$Y = Me_3Si$

$$Me_2SiX_2 + nD_4 \longrightarrow X(Me_2SiO)_{4n+1} \quad (31)$$

X = Cl, OR, OAc

Sulphuric acid is normally used in equilibration reactions but other mineral acids including chlorosulphonic acid and phosphoric acid and Lewis acids such as iron(III) chloride, aluminium chloride and boron trifluoride have been used successfully. The initial step in acid catalysed polymerisations is thought to be the attachment of a proton to an electron pair on a siloxane oxygen (equation 32).

$$\equiv Si\text{-}O\text{-}Si\equiv \xrightarrow{H^+} \equiv Si\text{-}\overset{+}{O}(H)\text{-}Si\equiv \qquad (32)$$

The subsequent reactions leading to the scission and reformation of siloxane bonds can be interpreted in two ways. The oxonium complex can decompose with the formation of an Si-OH bond and entails the reaction of an Si-X bond with the X^- anion

$$\equiv Si\text{-}\overset{+}{O}(H)\text{-}Si\equiv + X^- \longrightarrow \equiv Si\text{-}OH + \equiv Si\text{-}X \qquad (33)$$

and subsequent cleavage of the Si-O link. Both Si-OH and Si-X bonds can then react further to form new siloxane bonds. A series of bond scission and reformations follow to form a polysiloxane chain as a result of a favourable energy gradient, i.e.

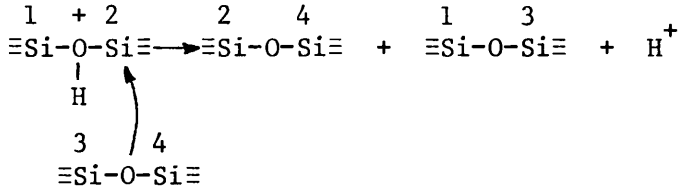
$$\equiv Si\text{-}OH + HO\text{-}Si\equiv \longrightarrow \equiv Si\text{-}O\text{-}Si\equiv + H_2O \qquad (34)$$

$$\equiv Si\text{-}X + H_2O \longrightarrow \equiv Si\text{-}OH + HX \qquad (35)$$

Alternatively, Si-OH and Si-X bonds can react further to regenerate the acid and form a new siloxane linkage (equation 36).

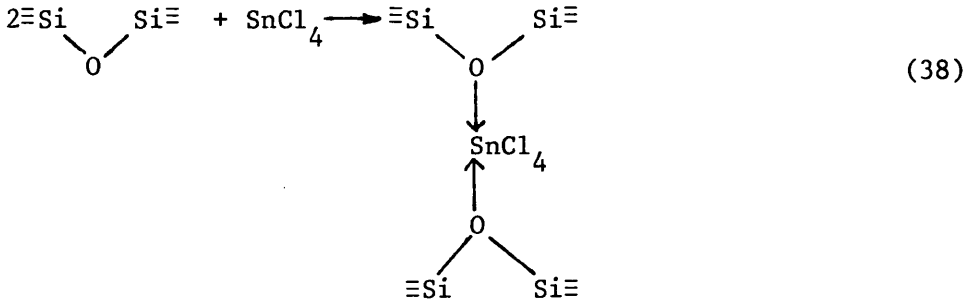
$$\equiv Si\text{-}OH + X\text{-}Si\equiv \longrightarrow \equiv Si\text{-}O\text{-}Si\equiv + HX \qquad (36)$$

Nucleophilic attack on the oxonium complex by a siloxane oxygen of an unprotonated molecule may also occur, followed by scission and re-formation of the siloxane bonds (equation 37).

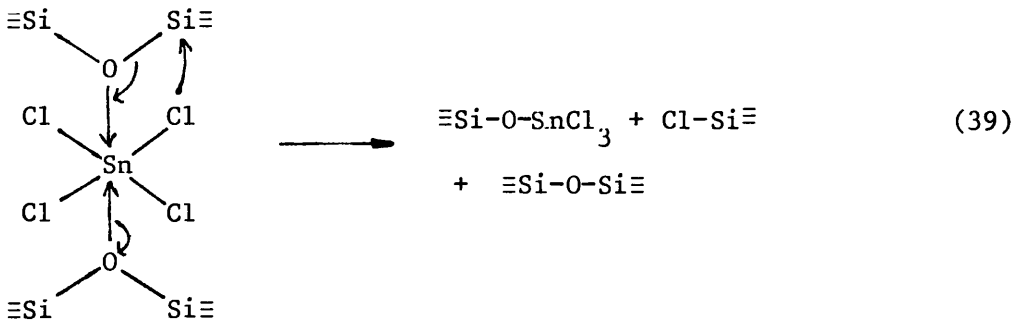


(37)

The mechanism for the action of Lewis acids such as $SnCl_4$ and $FeCl_3$ is similar to that of protic acids, and adducts of some Lewis acids, such as $SnCl_4$, with the siloxane bond in hexamethyldisiloxane have been isolated to support this mechanism[109]. This initial step is followed by cleavage of the siloxane bond, resulting in formation of a stannosiloxane bond.



(38)



(39)

In all these reactions, the reactivity of the Si-O-Si bond is strongly influenced by the nature of the organic groups or their substituents, with bulky aliphatic or aromatic substituents and electron acceptor groups decreasing the reactivity of the Si-O-Si bond.

The initial step in base catalysed reactions is nucleophilic attack at silicon which causes cleavage of the siloxane bond (equations 40, 41).

$$\equiv Si\text{-}O\text{-}Si\equiv \xrightarrow{OH^-} \equiv Si\text{-}O\text{-}\underset{\displaystyle OH}{\overset{\displaystyle -}{Si}}\equiv \qquad (40)$$

$$\equiv Si\text{-}\ddot{O}\text{-}\underset{\displaystyle OH}{\overset{\displaystyle -}{Si}}\equiv \longrightarrow \equiv Si\text{-}O^- + HOSi\equiv \qquad (41)$$

As a consequence of a favourable energy gradient, new Si-O-Si bonds are formed leading to rearrangement of the molecules and regeneration of the catalyst. Thus, in the case of potassium hydroxide, the following reactions occur. For both acid and base catalysis,

$$\equiv Si\text{-}O^- + K^+ \longrightarrow \equiv Si\text{-}OK \qquad (42)$$

$$\equiv Si\text{-}OK + HO\text{-}Si\equiv \longrightarrow \equiv Si\text{-}O\text{-}Si\equiv + KOH \qquad (43)$$

increasing the polarity of the solvent generally increases the concentration of $Si\text{-}O^-$ ions, and leads to a faster attainment of equilibrium.

The catalyst is normally removed on completion of polymerisation, because its presence would adversely affect the heat-ageing properties of the polymer, although removal may be difficult in the case of viscous fluids. Both acid and base catalysts are commonly removed by extraction with water. Homogenisers can be used to facilitate this process, or alternatively the polymer is first dissolved in an organic solvent which is immiscible with water, thus affecting phase separation. Alternatively, catalysts may be neutralised with reagents, yielding insoluble salts which may be filtered from the fluids, or products which remain soluble in the polymer.

1.2.3. PROPERTIES AND USES OF SILOXANES

Polysiloxanes are well-known for their thermal stability and inertness to various types of radiation as well as a wide range of chemicals[110,112]. Since their commercial introduction during World War II there has been a steady development in their applications based on characteristics that include a strong and flexible Si-O-Si link, a low energy barrier to Si-O rotation and low intermolecular forces. Important characteristics in addition to stability include good dielectric properties, low surface tension, transparency, film-forming ability, high permeability, biocompatability and water repellency (Table 1.8).

The differences between the R_2CO- and R_2SiO- moieties may be traced back to the electronic differences between C and Si. Unlike C, Si possesses relatively low energy vacant d-orbitals which may be used both to increase the coordination number of Si from 4 to 5 or 6, and to participate in $d\pi$-$p\pi$ bond formation with π-electron donor atoms

such as oxygen. Thus the Si-O σ-bonds in siloxanes are complemented by dπ-pπ bonding (which becomes more effective when the size of the dπ-silicon orbitals are contracted by electronegative substituents), and this contributes to the reduction in the Si-O separation from the calculated single bond value of 1.91Å to the observed value of 1.64±0.03Å. Heats of combustion measurements on organosiloxanes range from 420-490kJmol^{-1}, so confirming the high stability of the siloxane bond. The d-orbital participation in Si-O-Si bonding also results in a widening of the bond angle to ca. 130° and renders the bond strength relatively insensitive to changes in this angle, so accounting for the very wide variation reported in the SiOSi angle (ca. 100 - 170°) for various siloxanes[113].

Despite the good overall stability of polyorganosiloxanes, two types of reaction can contribute to severe property changes. A free radical reaction can occur in the presence of air (e.g. equation 44) resulting in homolytic cleavage of SiO, SiC or CH bonds and more serious degradation occurs in the presence of water, silanol, alcohol, acid or base (equation 45). The latter is particularly apparent when samples are held at high temperatures under confined conditions and is the primary mode of silicone degradation in the presence of traces of impurities.

$$\equiv Si\text{-}CH_3 \longrightarrow \equiv Si\text{-}CH_2 \longrightarrow \underset{\text{crosslinked polymer}}{\equiv Si\text{-}CH_2\text{-}CH_2\text{-}Si\equiv} \qquad (44)$$

$$\equiv Si\text{-}O\text{-}Si\equiv \xrightarrow{H_2O} 2\equiv SiOH \qquad \text{cyclic siloxanes} \qquad (45)$$

Organic polymers, when combined with silicones, often show improved stability compared with the pure organic polymer. This is due to the establishment of a heat resistant silicone matrix rather than by chemical stabilization of the alkyd.[114]

TABLE 1.8 APPLICATIONS OF POLYSILOXANES WHICH TAKE ADVANTAGE OF POLYMER STABILITY

Application	Type of Stability Required
Paints	UV radiation
Oil seal	Thermal, chemical
Oven gasket	Thermal
Nuclear reactor seals	Radiation
Roof coating	UV radiation
Solar collector sealant	Thermal, UV radiation

The mechanical properties of silicones can be tailored for a diverse variety of applications by proper use of cross-linking chemistry, fillers and other additives. A linear polymer which has been lightly cross-linked is in low modulus, resilient and quite weak when compared with other polymers, and materials which have found a wide range of commercial engineering uses almost all contain a second phase, often very small amorphous silica particles. Such particles commonly increase tensile strength by a factor of 35 and also raise the modulus. Recent investigations have shown that by arranging the crosslinks in a particular, non-random manner within the polymer network, unique properties can be developed. Patent literature shows that such networks confirm improved tensile strength, tear strength, toughness and solvent resistance[115].

Most mechanical applications require some other characteristic[116] in addition to the particular mechanical specification, and some typical applications are listed in Table 1.9.

TABLE 1.9 APPLICATIONS OF POLYSILOXANES DEPENDENT UPON RHEOLOGICAL PROPERTIES

Application	Property
Brake fluid	Viscosity, temperature relation
Liquid spring	Compressibility
Toys: 'silly putty'	Shear thickening
Sound damping	Complex viscosity

Most siloxane polymers act as very good insulators. The methyl groups are thought to shield the polar siloxane backbone, and in addition the hydrophobic nature of the surface repels water (and any dissolved ionic contaminants) which assures the retention of insulating properties under unfavourable conditions[117]. As expected the nature of the organic substituent strongly affects the electrical properties of the polymer with large hydrocarbon side groups (e.g. n-octyl) giving resistivities and dielectric constants similar to those of hydrocarbon fluids, whereas very polar groups (e.g. nitrophenyl) increase the dielectric constant by a factor of 8. The high diffusivity of silicones, combined with high transparency has also given rise to several interesting applications, some of which are listed in Table 1.10.

TABLE 1.10 APPLICATIONS OF POLYSILOXANES WHICH DEPEND ON PERMEABILITY

Application	Property
Continuous drug release	Drug permeability and biocompatibility
Fabric coating	Liquid water impermeability; high water vapour permeability
Contact lens	High O_2 permeability
Gas separation	Selective permeability of various gases
Fabric coating	Water liquid impermeability; High water vapour permeability

1.3. CATALYSIS BY POLYMER-SUPPORTED TRANSITION-METAL COMPLEXES

1.3.1. INTRODUCTION

Reactions relevant to studies reported in this thesis include hydrosilylation, oxidative coupling and dehydrogenation. In this section are outlined the basic mechanistic features of these reactions, and the effects, where known, of using supported rather than homogeneous catalysts.

1.3.2. HYDROSILYLATION

By definition, the hydrosilylation reaction consists of the addition of an $R^1R^2R^3Si$ unit (where R groups are typically alkyl, alkoxy or halide) and a hydrogen atom to an unsaturated molecule (equations 46 - 51).

e.g. $\equiv Si-H + \diagup C=C \diagdown \longrightarrow \equiv Si-\overset{\diagup}{\underset{\diagdown}{C}}-\overset{\diagup}{\underset{\diagdown}{C}}-H$ (46)

$\equiv Si-H + -C\equiv C- \longrightarrow \equiv Si-\overset{|}{C}=\overset{|}{C}-H$ (47)

$\equiv Si-H + \diagup C=O \longrightarrow H-\overset{\diagup}{\underset{\diagdown}{C}}-O-Si\equiv$ (48)

$\equiv Si-H + -C\equiv N \longrightarrow \equiv Si-N=CH-$ (49)

$\equiv Si-H + -N=O \longrightarrow -NH-O-Si\equiv$ (50)

$\equiv Si-H + -\overset{+}{N}\equiv\overset{-}{C} \longrightarrow -N=C\begin{matrix}H\\ \diagdown\\ Si\equiv\end{matrix}$ (51)

The hydrosilylation reactions of greatest commercial significance involve the addition of R_3SiH to an alkene and in the silicone industry, this reaction is of particular importance in the synthesis of cross-linking organofunctional silicon monomers.[118,119] Hydrosilylation reactions are usually accomplished by one of the following routes:

a) by heating the reactants together, usually at 300°C or higher under pressure,

b) by using a radical initiator, typically an organic peroxide or an azo-compound ,

c) by exposing the reactants to u.v.- or γ-radiation, or electrical discharge,

d) by catalysing the reaction with transition-metal salts or Lewis bases such as H_2PtCl_6, $Co_2(CO)_8$ or pyridine.

Of these the route (d) is most relevant to our studies and it has been suggested that at least in some supported catalyst systems reaction occurs at metal sites which remain bonded to the support during the reaction. This affects both the overall yields and selectivities found on using polymer anchored catalysts compared to their homogeneous analogues.[121]

The basic mechanisms for the free radical and platinum catalyzed additions[120] are given in Schemes 8 and 9 respectively.

Scheme 8

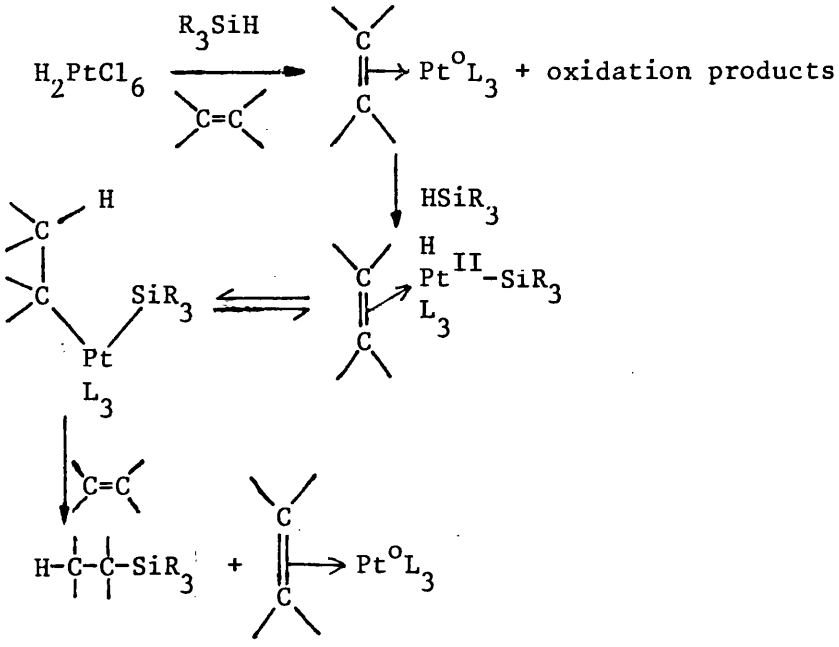
$$(\text{Initiator})_2 \longrightarrow 2\ \text{Initiator}^{\bullet} \quad (2I^{\bullet})$$

$$I^{\bullet} + HSiR_3 \longrightarrow IH + {}^{\bullet}SiR_3$$

$${}^{\bullet}SiR_3 + \text{>C=C<} \longrightarrow R_3Si\text{-}C\text{-}C^{\bullet}$$

$$R_3Si\text{-}C\text{-}C^{\bullet} + R_3SiH \longrightarrow R_3Si\text{-}C\text{-}CH + R_3Si^{\bullet}$$

Scheme 9



The ease of metal catalysed additions depends in general on (a) the alkene, (b) the catalyst, and (c) the solvent and reaction conditions. The presence of electron-withdrawing substituents on the alkene will reduce reactivity, this effect being related to the ease of initial complex formation. Speier's catalyst[119], $H_2PtCl_6.6H_2O$, which is effective at very low concentrations, is the catalyst of choice for the hydrosilylation of unactivated alkenes, though many other transition-metal complexes containing Rh, Pd, Ni, Co or Fe will also catalyst this reaction to some extent. The addition process can tolerate a wide variety of functional groups on both carbon and silicon, but a strong steric influence is noted with silicon bonding to the less hindered end of the alkene. As a consequence terminal alkenes are hydrosilylated more readily than internal alkenes, which are known to isomerize prior to addition so yielding terminal products in many instances.[122]

e.g. 3-heptene $\xrightarrow{HSiR_3}$ 1-heptene $\xrightarrow{HSiR_3}$ $n\text{-}C_7H_{15}SiR_3$ (52)

An optically active silane retains its configuration on addition, and asymmetric induction has been observed in the hydrosilylation reaction of ketones and alkenes on using homogeneous catalysts that bear chiral ligands.[123] In an attempt to define more precisely the nature of the platinum species formed in homogeneous catalytic cycles, Chandra et al[124] studied the reaction of sym-tetramethyldivinyldisiloxane with Speier's catalyst. The formation of the Pt(0) solution species $[Pt\{\eta^4\text{-}Me_2ViSiO(Me_2SiO)_xSiMe_2Vi\}_y]$ (XVIII) (Vi = vinyl; x = 0-14, but mainly x = 0; and y = 2-4, but mainly y = 2), was inferred from cyclic voltammetry, nmr methods and gas chromatography.

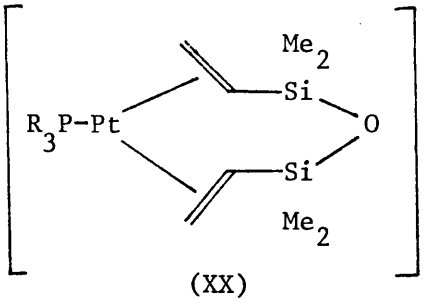
Both bis(η^2-alkyne)platinum(0) (XIX) and (tertiary phosphine) platinum(0) (XX) complexes were synthesised using solutions of(XVIII). X-ray data on (XX) (R = t-Bu) showed that $(Me_2ViSi)_2O$ behaves as a chelating bidentate ligand.

$[Pt(\eta\text{-}RC{\equiv}CR^1)_2]$

(XIX)

(R = Ph, CMe_2OH

R^1 = CMePhOH, Ph, CMe_2OH)

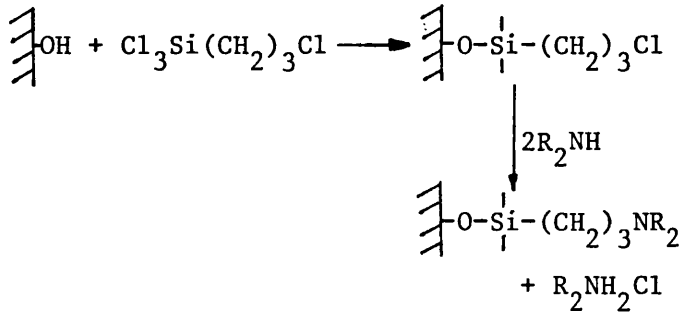


(XX)

R = t-Bu, Cy

In recent studies on supported metal catalysed hydrosilylation reactions, Marciniec et al[125] prepared platinum and rhodium catalysts which were bonded to silica via amine functionalities (morpholine, piperidine, diethylamine, diphenylamine, or pyrrolidine), as illustrated in Scheme 10.

Scheme 10



where, R_2 = $(C_2H_4)_2O$, $c\text{-}C_5H_{10}$, $c\text{-}C_4H_8$, $(C_6H_5)_2$, $(C_2H_5)_2$

The various N-bases had little effect on the activities of the catalysts in hydrosilylation reactions nor were the amine-metal ratios very significant in this context. In a later publication[126], the same research group prepared soluble silylphosphine and insoluble polysiloxyalkylphosphine supports to which were anchored rhodium complexes (XXI and XXII respectively).

$[Ph_2P(CH_2)_xSi(OEt)_3]RhCl$ and $[O_{3/2}Si(CH_2)_xPPh_2]_yRhCl(PPh_3)_n$

(XXI) (XXII)

(x = 2 or 3)

The activity of (XXI) for the hydrosilylation of 1-hexene by triethoxysilane was found to be very similar to that of Wilkinson's complex $RhCl(PPh_3)_3$, but the polymeric analogues (XXII) (x = 2 and 3) gave different yields of products (84 and 58% respectively) compared to $RhCl(PPh_3)_3$ (72%) when used under identical conditions. Kinetic data was reported, and the authors concluded that the differences in behaviour related to differences in electronegativity between the phosphine substituents.

The most recent paper in this series describes the preparation of rhodium siloxyphosphine catalysts by equilibrating $[RhCl(COD)]_2$ solutions (COD = cyclooctadiene) with 1,3-bis(ω-diphenylphosphinoalkyl)-tetramethyldisiloxanes, i.e. $O[Si(CH_3)_2(CH_2)_nPPh_2]_2$ (n = 1,2,3) so yielding catalysts B-1, B-2 and B-3 respectively or 1,3,5-tris-2-(diphenylphosphino)ethylpentamethyltrisiloxane which yielded catalyst C.

The authors also prepared the PPh_3 analogue from the octadiene rhodium complex (catalyst A), and compared the activities of all these with that of $[RhCl(COD)]_2$ (catalyst D) and Wilkinson's catalyst, $RhCl(PPh_3)_3$ (catalyst E) for the hydrosilylation of 1-hexene by triethoxysilane. A slight decrease in turnover number for catalysts A, B and C was observed compared with catalyst (E) but the activation energies for the rhodium-siloxy-phosphine complexes (B and C) were a little higher than those for the rhodium phosphine complexes A and E. Thus a summary of these studies reveals that subtle differences do exist between homogeneous hydrosilylation catalysts and their polysiloxane supported analogues, although to date relatively little work on systems other than Rh and Pt has been published.

1.3.3. HYDROGENATION

Hydrogenation reactions of organic substrates can be catalysed by an extremely large number of diverse heterogeneous and homogeneous transition-metal systems, as indicated in many books and reviews[128-130]. Some of the most active heterogeneous catalysts also lack specificity, and give rise to competing reactions such as isomerisation and hydrogenolysis. Homogeneous catalysts are more easily controlled to give good selectivity, and some of the most useful and highly studied species are based on the d^8-metal complexes of rhodium(I), iridium(I), platinum(II) and palladium(II). The role of the metal centre in transition-metal salt catalysed homogeneous hydrogenation reactions of alkenes consists of three functions;

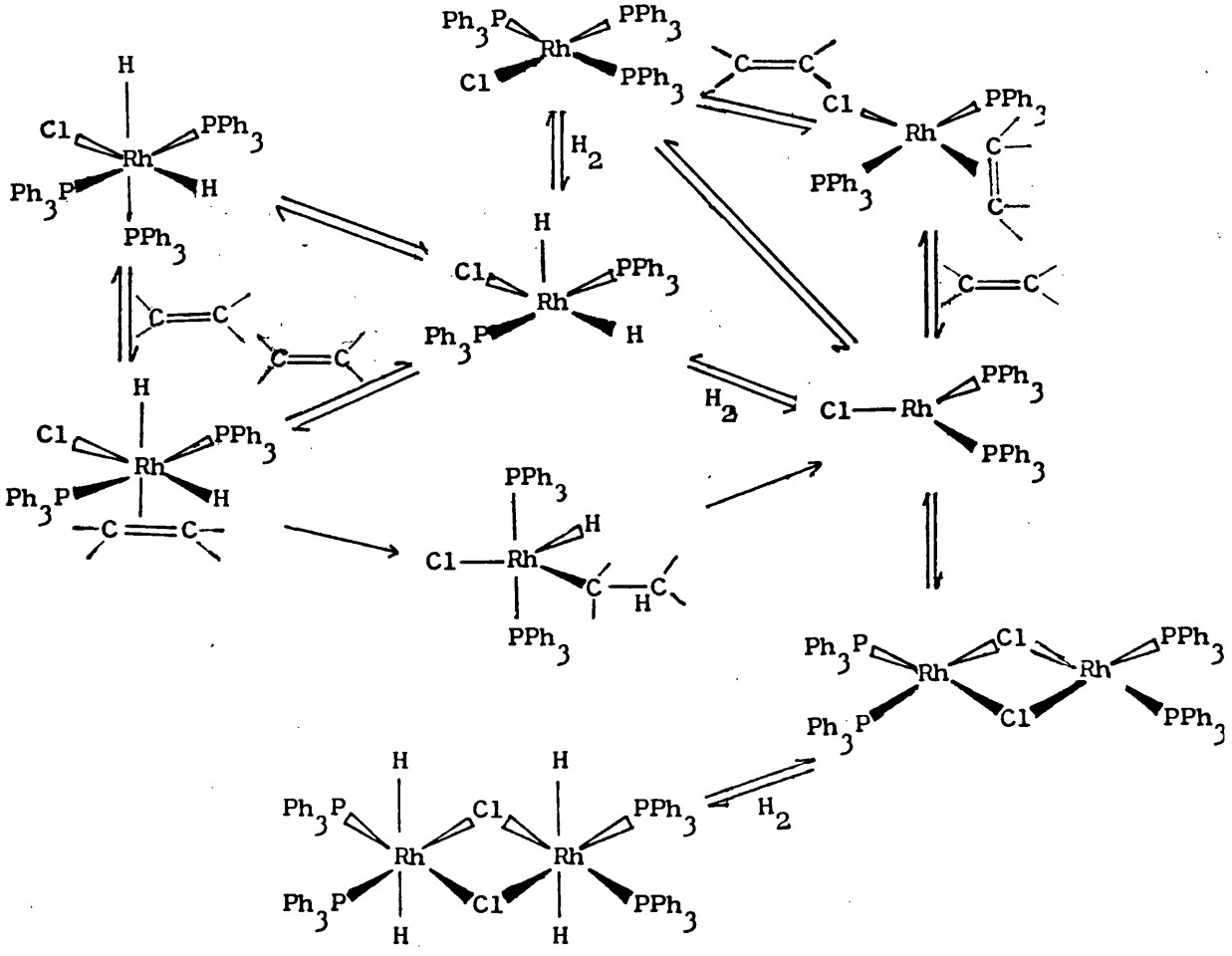
a) the metal provides a low energy means of activating dihydrogen, usually by an oxidative addition process,

b) the metal coordinates the alkene in a vacant site, thereby activating and positioning the substrate for subsequent reaction, and

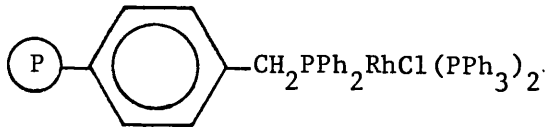
c) the metal provides the electronic environment for the addition of hydrogen to the alkene carbon atoms so yielding an alkane, and regenerating a catalytically active species.

Wilkinson's catalyst $RhCl(PPh_3)_3$ is widely used and the simplified mechanism for the homogeneous hydrogenation of alkenes is outlined in Scheme 11.

Scheme 11



In polymer supported hydrogenation catalyst systems, increasing the degree of cross-linking in the support has been shown to generally decrease the activity of a catalyst[1], but the specificity is often increased since the polymer chains are bound tightly together and so entry to the interior catalyst sites may be restricted to small substrates. The type of solvent used can also have profound effects by influencing the degree of polymer swelling, and hence affecting activity and selectivity. These influences have been particularly well demonstrated in polystyrene supported Wilkinson catalyst analogues of the type (XXIII)[131,132], and for catalysts prepared by treating (P)-PPh_2 with $[RhCl(\eta^2\text{-}C_2H_4)]_2$ [133], and



(XXIII)

{poly[1,6-bis(p-toluene sulphonate)-2,4-hexadiyne]}-PPh_2 and $[RhCl(C_8H_{14})_2]_2$ [134].

In 1976, Conan et al[135] described a support for rhodium complexes which yielded more active hydrogenation catalysts than its homogeneous analogues, or any other related supported catalyst. Polyphenylsiloxane was first prepared by hydrolysis of phenyltrichlorosilane. This low molecular weight prepolymer was then used directly to cover silica by reacting it in the presence of large or catalytic amounts of KOH, which resulted in the formation of polycyclic compounds such as octaphenylsilsesquioxane or high polymers of ladder polyphenylsiloxane respectively on the oxide surface. Rhodium was anchored to these by ligand displacement from the Cramer complex

$[RhCl(\eta^2\text{-}C_2H_4)_2]_2$[136]. The exceptional activity of this material reflected a fundamental change in the nature of the anchored rhodium species during hydrogenation, which was shown[137] to involve the formation of dispersed metallic rhodium. A number of supported complexes derived from $[RhCl(CO)_2]_2$ supported on phosphinated silicas behaved similarly, and the formation of metallic rhodium has been inferred subsequently in some other hydrogenation studies[138,139].

Studies on the activity of $RhCl(PPh_3)_3$ supported on styrene-divinylbenzene[140] have shown that the rates for reduction of cyclohexene, styrene and 1-hexene are lower than those for the analogous homogeneous catalyst. The ratio between the rate of reduction of 1-hexene and of cyclohexene is higher, however, than that in the homogeneous phase. This increased selectivity was attributed to steric hinderance around the active sites on the resin, as described earlier for hydrosilylation reactions. In agreement with this observation, decreases in rate are associated with reduction occurring on metal sites on inner phosphine groups of the copolymer.[141]

1.3.4. DEHYDROGENATION

Dehydrogenation catalysts function in a reverse manner to hydrogenation catalysts. Thus complexes of general formula $Ru(CO)(O_2CCF_3)_2(PR_3)_2$ convert alcohols to aldehydes or ketones, and the catalytic cycle in this case includes the hydrido-species $RuH(CO)(O_2CCF_3)(PR_3)_2$, from which CF_3CO_2H regenerates the dicarboxylato complex with the evolution of dihydrogen. Shinoda et al[142] recently reported the first example of thermal dehydrogenation of methanol in

solution with a homogeneous ruthenium complex (XXIV). This is an endothermic reaction and gives a product free from water, although

$[Ru(OAc)Cl(PR_3)_3]$

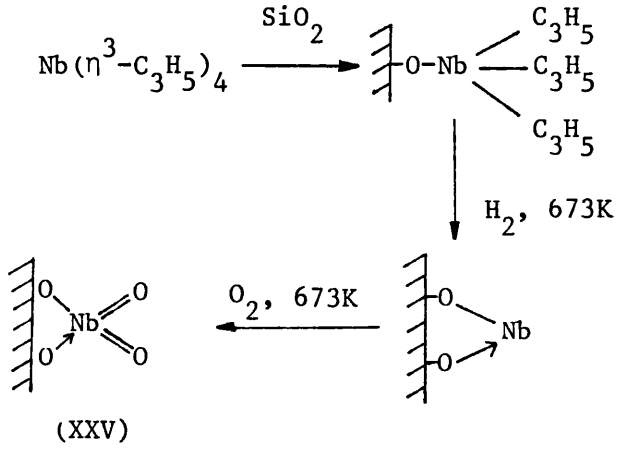
(XXIV)

(PR_3 = PPh_3, $PEtPh_2$)

as the reaction proceeds, the initial product formaldehyde (and its dimethyl acetal) are gradually converted into secondary products including methyl formate. Previous homogeneous, transition metal catalysed dehydrogenations of methanol have only been carried out efficiently under photocatalytic conditions[143], although homogeneous dehydrogenation of primary and secondary alcohols with higher chain lengths ($>C_2$) have been reported previously[144,145].

A range of polymer-supported complexes are known which catalyse this type of reaction (Table 1.11). A combination of high activity and selectivity can be achieved for the dehydrogenation of ethanol by using Nb(V) monomers supported on SiO_2, Al_2O_3 or TiO_2[146] (Scheme 12).

Scheme 12



(XXV)

This reaction is in contrast to the preferential dehydration to form predominantly ethene and diethyl ether observed over the more usual Nb impregnated catalysts.

Dehydrogenation reactions of alkenes have been observed using a polymer-supported palladium acetate catalyst formed by wet impregnation of an insoluble co-oligomeric species, oligo-p-phenyl-eneterephthalimide (OPTA) with a water-acetic acid solution of palladium acetate[147]. In the presence of oxygen and perchloric acid in ethanol-water conversion of terminal and internal monoalkenes into the corresponding alkynes was achieved under mild conditions and in high yields. Wacker-type ketonization occurs with the same reagent in dioxane-water.

TABLE 1.11 POLYMER SUPPORTED DEHYDROGENATION CATALYSTS

Polymer type	Support functionality	Metal Complex or Species supported
Polystyrene	$-CO_2H$	$Ru(O_2CCF_3)_2(CO)(PPh_3)_2$
Polystyrene	$-PR_2$	$Ru(O_2CCF_3)_2(CO)(PPh_3)_2$
Pyrolyzed poly(acrylonitrile)	P -CN	$Ni(OAc)_2$, H_2PtCl_6
Poly(naphthoquinone)	$\rangle C{:}$	$TiCl_4$, $FeCl_3$, VCl_3, $Mo(CO)_5$

1.3.5. HYDROFORMYLATION AND CARBONYLATION REACTIONS

The addition of CO to organic substrates is catalysed by many soluble metal compounds, and these reactions are useful for the formation of a wide range of compounds including carboxylic acids, acid halides, ketones and isocyanates (equations 53 - 56).

e.g. $ROH \xrightarrow{CO} RCO_2H$ (53)

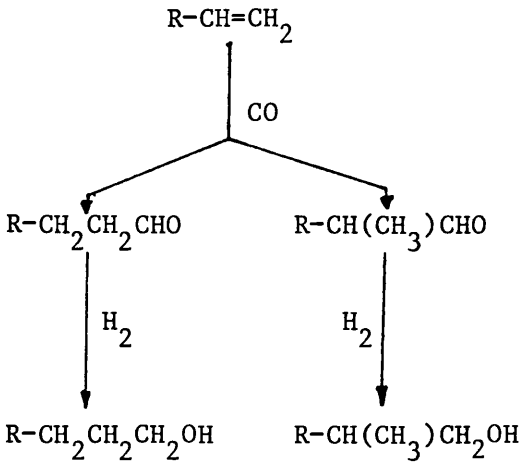
$RX \xrightarrow{CO} RCOX$ (X = halide) (54)

$RNH_2 \xrightarrow{CO} RNHCHO$ (55)

$RNO_2 \xrightarrow{CO} RNCO$ (56)

One of the most important carbonylation reactions involves the formation of mixtures of isomeric aldehydes (together with some alcohols) by the simultaneous addition of CO and H_2 to an alkene. Such reactions frequently employ Co and Rh complexes.

Scheme 13



(normal, n) (iso, i)

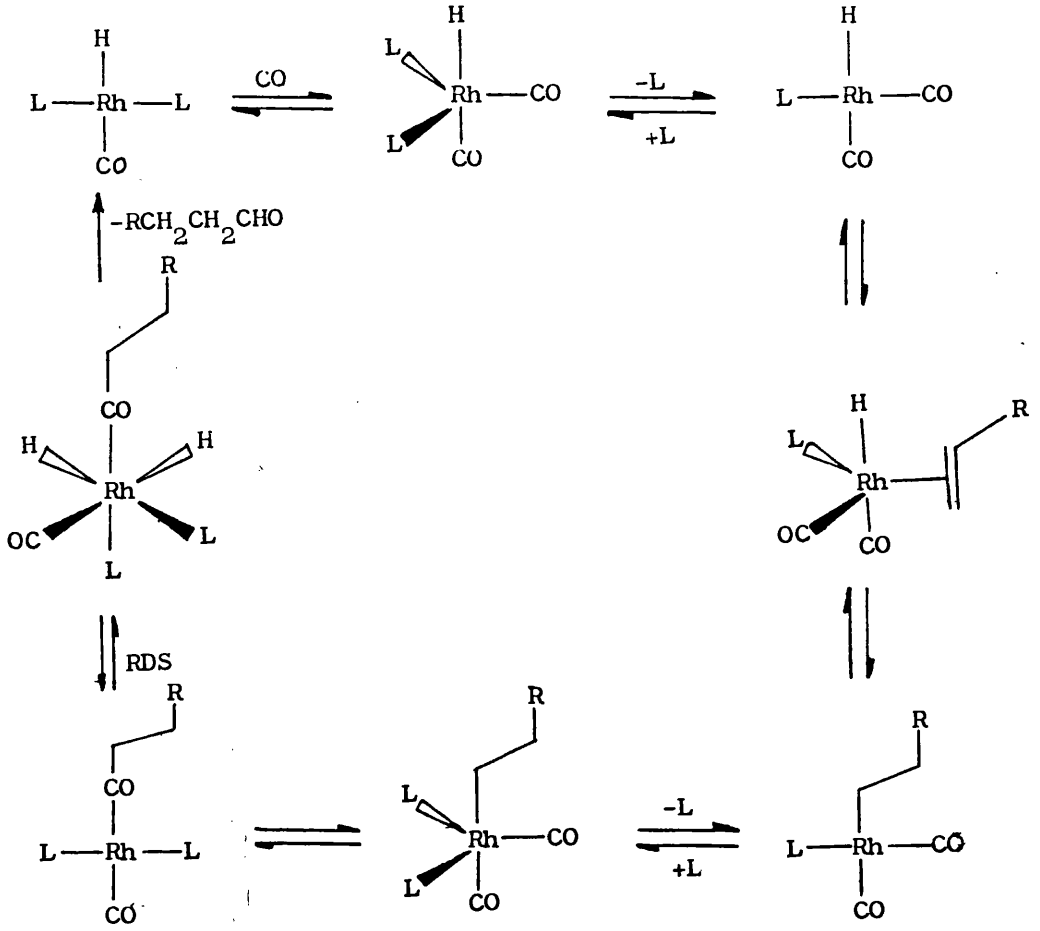
Rhodium catalysed alkene hydroformylation reactions have been extensively studied by Wilkinson et al,[148,149] who postulated two mechanisms (Scheme 14) to explain the essential characteristics of the reaction. One mechanism was an associative process involving attack by hydrogen on the monomeric $Rh(CO)_2(PPh_3)_2$ complex, whilst the other is described as a dissociative process involving initial loss of a triphenylphosphine ligand from $[RhH(CO)_2(PPh_3)_2]$. Oxidative cis-addition of H_2 to a square planar rhodium(I) complex is assumed to be the rate determining step in each mechanism. The authors concluded that both mechanisms can function under the same conditions. Excess phosphine favours the associative mechanism, whilst the dissociative pathway can operate in the absence of additional phosphine or with high partial pressures of CO. Thus, higher n:i ratios are observed in the presence of additional phosphine (Scheme 14).

A matrix bound rhodium(I) complex, formed by a ligand exchange reaction between $[Rh(CO)Cl(PPh_3)_2]$ and the diphenylphosphino residue on a styrene-divinylbenzene copolymer, has been used as a supported catalyst for the carbonylation reaction of methanol in the presence of methyl iodide.[150]

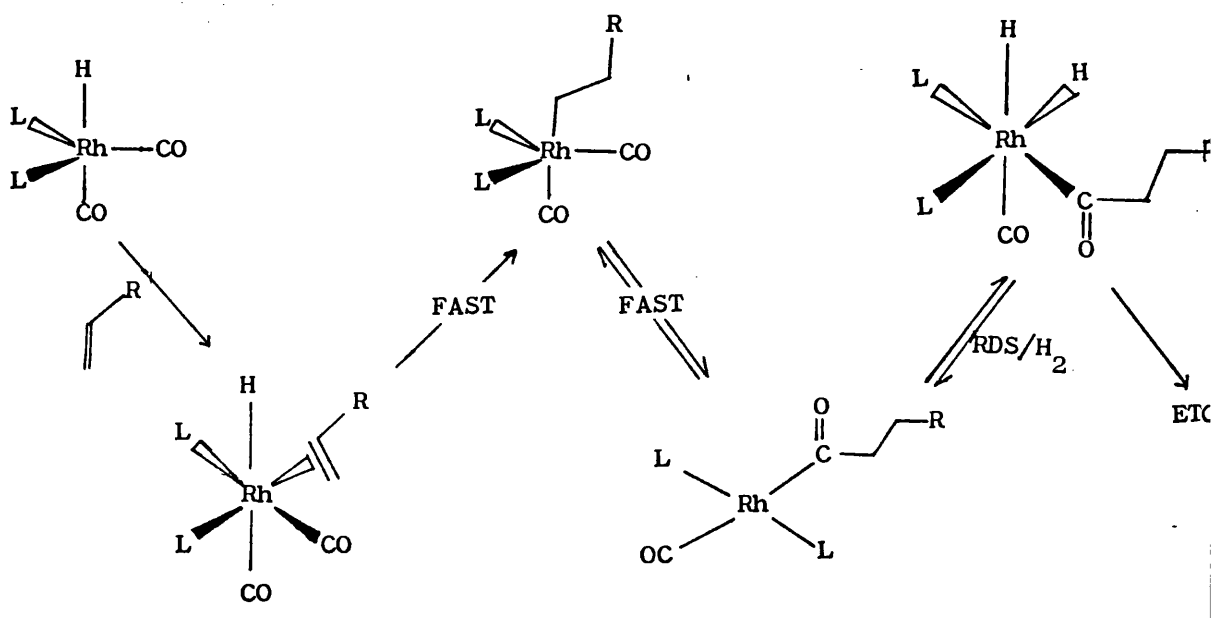
The reaction was found to be second order, while that involving the homogeneous complex $[Rh(CO)Cl(PPh_3)_2]$ was first order. The mechanism outlined in Scheme 15 was proposed as a result of these studies, however, the activity of the catalyst was found to progressively diminish as a result of the irreversible conversion of Rh(I) to Rh(III). Rhodium catalysts attached to macroreticular amine

Scheme 14

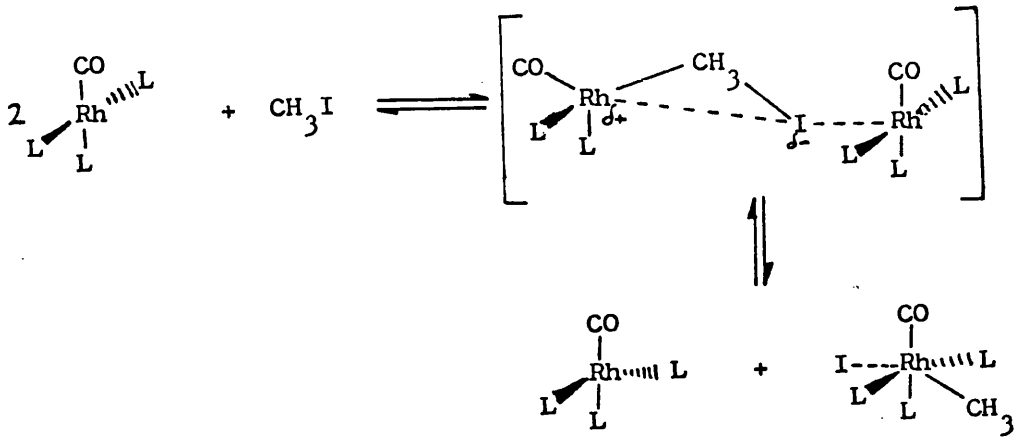
Dissociative Path



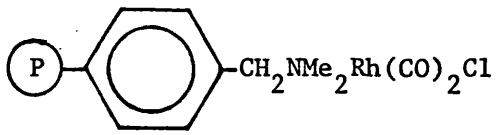
Associative Path



Scheme 15



resins, such as (XXVI), have shown substantially higher selectivities

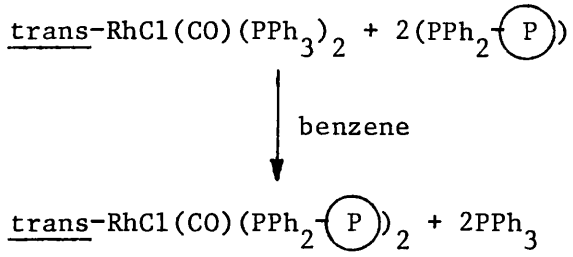


(XXVI)

in the hydroformylation of α-alkenes at increased temperatures and pressures compared with homogeneous dimethylbenzylamine analogues.[151,152] Various other polymer-attached ligands have also been used to support rhodium catalysts but the linear:branched product selectivity was not sensitive to the nature of the ligand with either resin supported or homogeneous catalysts.

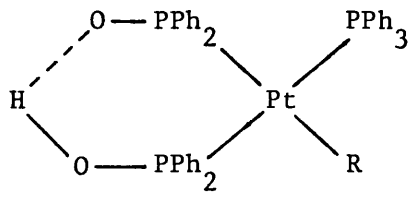
Farrel et al[86,153] treated a series of poly(methylsiloxanes) containing carbon-functional diphenylphosphine groups with

[RhCl(CO)$(PPh_3)_2$] to produce polymer-attached chlorocarbonylrhodium(I) complexes.



(57)

The two metallated complexes derived from a phosphinated silicone polymer containing one-PPh_2 group per 60 siloxy units, and one-PPh_2 group per 20 siloxy units, were found to be very active catalysts for the hydroformylation of hex-1-ene at elevated temperatures and pressures yielding linear:branched heptaldehydes in a ratio of 1:0.9. However, both rhodium and phosphorus were lost from the polymers and the actual catalyst appears to be a homogeneous rhodium carbonyl species. The same reaction has been studied by Leeuwen et al[154] using platinum complexes of the type [Pt(H)$(Ph_2PO)(Ph_2POH)(PPh_3)$] (XXVII). These yielded products of high linearity (90%) and intermediate alkyl and acyl complexes (XXVIII) were successfully isolated and identified.



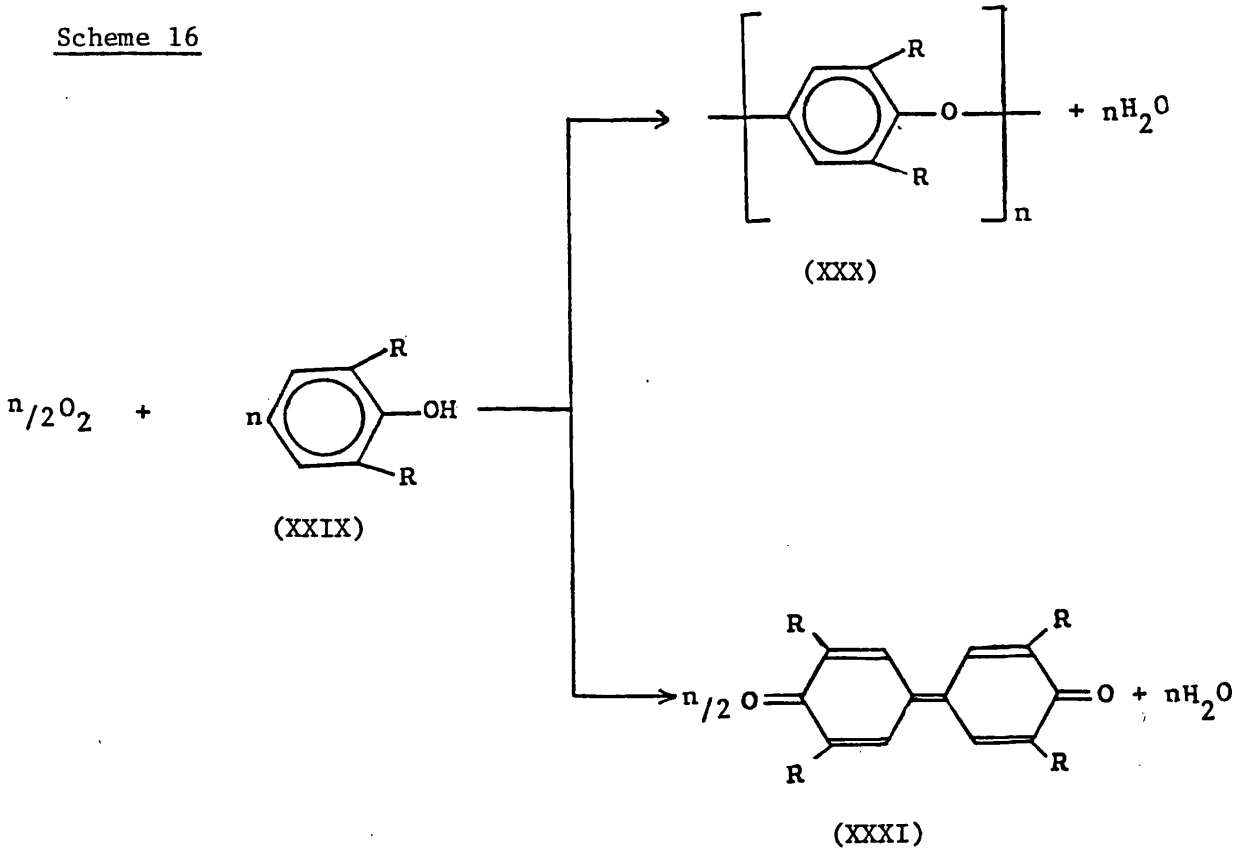
(R = Et, COEt, COPr)

(XXVIII)

1.3.6. OXIDATIVE COUPLING REACTION

It is well-established[155,156] that certain hydroxyphenyl compounds, notably 2,6-disubstituted phenols, can be oxidatively polymerised to yield high molecular weight polyphenylene ethers (XXX) or diphenoquinones (XXXI) by means of molecular oxygen in the presence of basic copper salt-tertiary amine catalysts (Scheme 16).

Scheme 16



Endres and co-workers[157,158,159] have shown that this reaction can be controlled to give either carbon-oxygen or carbon-carbon coupled major products. The nitrogen-copper ratio has a significant effect on the course of the reaction, however, a complete mechanistic understanding of the course of the reaction is not known. The authors postulated that an early mechanistic step involved oxidation of copper(I) chloride to $[CuCl(OR)(amine)]_2$, or an analogue (equations 58 and 59). Two

different reaction sequences occurred in MeOH-pyridine solutions depending upon the pyridine:copper ratio

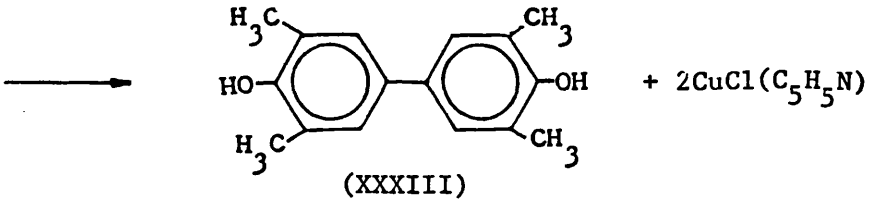
$$4CuCl + O_2 + 4CH_3OH + 4C_5H_5N \rightarrow 2[CuCl(OMe)(C_5H_5N)]_2 + 2H_2O \qquad (58)$$

$$[CuCl(OMe)(C_5H_5N)]_2 + ROH \rightarrow [CuCl(OR)(C_5H_5N)]_2 + 2\ MeOH \qquad (59)$$

(XXXII)

At a pyridine:copper ratio of 1 (XXXII) undergoes a metathesis with 2,6-dimethylphenol (XXIX) so yielding 3,3',5,5'-tetramethyl-4,4'-dihydroxydiphenyl (XXXIII) (equation 60). Subsequent oxidation of

(XXIX) + (XXXII)



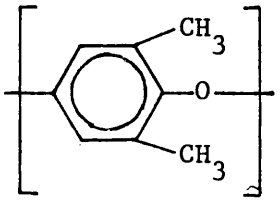
(XXXIII) + $2CuCl(C_5H_5N)$ (60)

(XXXIII) by either oxygen or copper(II) leads to tetramethyldiphenoquinone (XXXI), and oxidation of copper(I) species regenerates $[CuCl(OR')(C_5H_5N)]_2$.

$$4CuCl(C_5H_5N) + 4R'OH + O_2 \rightarrow [CuCl(OR')(C_5H_5N)]_2 + H_2O \qquad (61)$$

At pyridine:copper ratios greater than 10, the initially copper species undergoes a further reaction to yield $CuCl(OMe)(amine)_2$. Subsequent steps involve the replacement of the methoxy group by 2,6-dimethylphenoxide, and reduction of copper(II) to copper(I) with concurrent oxidation of the phenoxide to phenylene ether

$$CuCl(OMe)(amine)_2 + ROH \rightarrow CuCl(OR)(amine)_2 + CH_3OH \qquad (62)$$

$$nCuCl(OR)(amine)_2 \rightarrow \left[\text{  }\right]_n + nCuCl(amine)_2 + {}^{n}/_{2}H^{+}$$

$$4CuCl(amine)_2 + O_2 + 4HOR' \rightarrow CuCl(OR')(amine)_2 + 2H_2O \qquad (63)$$

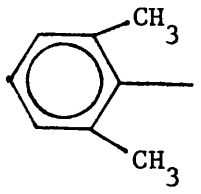
R =  ; R' = R or CH_3

Table 1.12 contains examples of polymer supported metal complexes that catalyse the oxidative coupling of ethynylbenzene[4].

TABLE 1.12 POLYMER SUPPORTED CATALYSTS FOR THE OXIDATIVE COUPLING OF ETHYNYLBENZENE

Polymer Type	Support Functionality	Supported Metal Species
Polyacrylates	O P -CO-	Ag^+
Cation exchange resin	Ionic	$NaHWO_4$

1.4. RESEARCH PROGRAMME USING SILOXANE-SUPPORTED TRANSITION-METAL SPECIES

The research programme which forms the basis for the work described in this thesis can be summarised as follows;

a) the synthesis and characterisation of a range of organofunctionalised model siloxanes and polysiloxanes,

b) the preparation of selected transition-metal entities for coordination to the functionalised polysiloxanes, and

c) the characterisation, and evaluation of the metallated polymers as homogeneous catalysts towards hydrosilylation, oxidative coupling and dehydrogenation reactions.

CHAPTER 2

SYNTHESIS OF FUNCTIONALISED ORGANOSILOXANES

2.1. SUMMARY

A range of linear organofunctionalized polysiloxanes with a varying degree of polymerisation and mole percent functionality have been synthesised. Ligand endings incorporated in the polymers include the 3-aminoethylamino (subsequently referred to as ethylenediamino), alkenyl, cyclohexenyl, aryl, 4-carboxy-2-thiabutyl, alkyl- and arylthio, and diphenylphosphino entities. These are all capable of complexing transition metal species.

$$Me_3SiO(Me_2SiO)_x(MeSiO)_ySiMe_3$$
$$\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\quad R$$

R = $-(CH_2)_3NH(CH_2)_2NH_2$, $-CH=CH_2$, $-(CH_2)_4CH=CH_2$, $-(CH_2)_2C_6H_9$, $-(CH_2)_3C_6H_5$, $-(CH_2)_2SCH_2COOH$, $-(CH_2)_3SH$, $-H$, $-(CH_2)_2PPh_2$, $-(CH_2)_2SPh$, $-(CH_2)_2SBu$, $-(CH_2)_6PPh_2$, $-(CH_2)_6SPh$

Model organosiloxanes have also been prepared for metallation and spectroscopic comparison with metallated linear siloxane polymers (Chapter 5). Thus tri-, tetra- and penta-siloxanes with a vinyl functionality were first prepared, and the tri-siloxane derivative was subsequently converted into diphenylphosphino- and arylthio containing species.

$$Me_3SiO(MeSiO)_nSiMe_3$$
$$\qquad\quad |$$
$$\qquad\quad R$$

R = H, n = 1; $-CH=CH_2$, n = 1, 2 and 3; $-(CH_2)_2PPh_2$, n = 1; $-(CH_2)_2SPh$, n = 1.

Full characterisation of these siloxanes and of relevant starting materials has been carried out using infrared and nuclear magnetic resonance methods, and polymer molecular weights have been determined by gel permeation chromatography as described in Chapter 3.

2.2. SYNTHETIC PROCEDURES

2.2.1 MODEL ORGANOSILOXANES

The synthetic procedures used were generally similar to those reported earlier[160]. Thus organic functionalities were introduced either via ≡Si-H addition to substituted alkenes in order to generate ≡Si-$(CH_2)_n$-L moieties, or by photochemical addition of HL to a ≡SiCH=CH_2 group. The trisiloxane starting material $Me_3SiO(MeSi(H)O)SiMe_3$ (I) was prepared by equilibration of $Me_3SiO[MeSi(H)O]_nSiMe_3$ (n≃40) and $(Me_3SiO)_2O$ employing trifluoromethanesulphonic acid as catalyst, and was separated from other products (table 2.4) by distillation at atmospheric pressure.

Model siloxanes $Me_3SiO[Me_2Si(CH=CH_2)O]_nSiMe_3$ (n = 1, 2 and 3) containing the vinylic ligand ending were prepared as recently described by Brisdon and Watts[160], via the hydrolysis of commercially available dichloromethylvinylsilane $SiMeCl_2(CH=CH_2)$ in the presence of chlorotrimethylsilane (equation 64).

$$SiMeCl_2(CH=CH_2) \xrightarrow[H_2O]{Me_3SiCl} Me_3SiO\left[\begin{array}{c} Me \\ | \\ Si-O \\ | \\ CH=CH_2 \end{array}\right]_n SiMe_3 \qquad (64)$$

(n = 1, 2 and 3)

Ether extraction followed by fractional distillation under reduced pressure permitted separation of each of the first three members of the series, following removal of hexamethyldisiloxane formed as a by-product during hydrolysis. The tetrasiloxane was obtained as the major product from the reaction which was carried out at low temperature in order that the liberated HCl did not cause significant cleavage of the Si-O bonds. All three vinyl functionalised compounds were obtained as air-stable colourless oils.

By using an analogous procedure to that described by Brzezinska and Cullen[83], phosphino and thio functionalised trisiloxanes [(4) and (5)] were synthesised in quantitative yield by the photochemical addition of diphenylphosphine, thiophenol or butanethiol respectively to the vinyl trisiloxane (equation 65).

$$Me_3SiO[MeSi(CH{=}CH_2)O]SiMe_3 \xrightarrow[h\nu]{HX} Me_3SiO[MeSi(CH_2CH_2X)O]SiMe_3 \qquad (65)$$

$$(X = PPh_2,\ SR)$$

The phosphine functionalised trisiloxane (3) was isolated as an air sensitive colourless oil which proved to be pyrophoric, whereas the arylthio and alkylthio functionalised species (4) and (5) respectively were air-stable, clear, yellow oils.

TABLE 2.1 MODEL FUNCTIONALISED SILOXANES $Me_3SiO[MeSi(R)O]_nSiMe_3$

	n	R
(1)	1	H
(2a)	1	$CH=CH_2$
(2b)	2	$CH=CH_2$
(2c)	3	$CH=CH_2$
(3)	1	$CH_2CH_2PPh_2$
(4)	1	CH_2CH_2SPh
(5)	1	CH_2CH_2SBu

2.2.2. FUNCTIONALISED ORGANOPOLYSILOXANES

One or more of several synthetic procedures were employed for the preparation of the organofunctionalised polysiloxanes listed in Table 2.2. These included;

a) base catalysed equilibrations,

b) acid catalysed equilibrations, and

c) modification of either commercially available polymers or functionalised polymers as prepared by methods under a) or b) above.

The following materials were provided by Dow Corning Limited and have been used as starting materials either directly or following purification by fractional distillation.

CYCLIC SILOXANES: $(Me_2SiO)_4$

$[MeSi(CH{=}CH_2)O]_4$

$[MeSi(CH_2CH_2SCH_2COOH)O]_4$

OTHER FUNCTIONALISED MATERIALS: $HO[Me_2SiO]_nH$ (hydrolysate) (n≃48)

$(MeO)_2MeSi(CH_2)_3NH(CH_2)_2NH_2$

$(MeO)_2MeSi(CH_2)_3SH$

$Me_3SiO[MeSi(H)O]_nSiMe_3$ (n≃40)

$Me_3SiO[Me_2SiO]_3[MeSi(H)O]_5SiMe_3$

POLYMER CHAIN ENDBLOCKERS: $(Me_3Si)_2O$

$Me_3SiO[Me_2SiO]SiMe_3$

$Me_3SiO[Me_2SiO]_2SiMe_3$

In all of the polymerisation procedures described in this chapter, the equilibration of the reactants was taken to be complete when viscosity and/or gel permeation chromatography determined molecular weights became constant. Viscosity measurements during equilibrations were monitored simply by means of a pipette and stopwatch.

The desired degree of polymerisation (D.P.) and mole percentage (mol %) of the polymers were obtained by varying the ratios of the starting materials. Thus in the synthesis of the ethylenediamine functionalised polysiloxanes (5a-d), $Me_3SiO[Me_2SiO]_x[MeSi(CH_2CH_2CH_2NHCH_2CH_2NH_2)O]_ySiMe_3$ the chain length of the polymer (or degree of polymerisation) is determined by the ratio of hydrolysate to the endblocker. For a 50 D.P. polymer:

$$D.P. = x + y + 2 = 50$$

The ratio of the hydrolysate to ethylenediamine functionalised

silane $(MeO)_2MeSi(CH_2)_3NH(CH_2)_2NH_2$ determines the mole percent of amine in the polymer. For a 50D.P. 4mol% polymer.

$$y = \text{mol\%} \times \frac{D.P.}{100} = 4 \times \frac{50}{100} = 2$$

The use of dicalite as a filter-aid facilitates the removal of neutralised acid (used as a catalyst) and all precipitated material from the fluid product.

The overall composition of a given polymer was confirmed by carbon and hydrogen analyses and in appropriate cases nitrogen and halide determinations. Viscosities for a selection of the polymers produced in quantity have been measured by means of a U-tube viscometer. Values given in the experimental section are average values determined several times on different preparations of each particular D.P. and mol% functionalised material. In general it was found that the viscosity of a functionalised polysiloxane increases with increasing D.P. and mol% functionality. The cyclic siloxanes, employed as starting materials have been described in the text as $[MeSi(R)O]_4$ (R = Me, CH = CH_2, $CH_2CH_2SCH_2COOH$). The tetramer with R = $CH{=}CH_2$ was shown by gas chromatography to be the most abundant component (ca. 78%) in the commercial sample of $[MeSi(CH{=}CH_2)O]_n$. Other cyclics with n = 3, 5 and 6 together with some linear material were also present in relatively small quantities. Fractional distillation yielded almost pure tetramer which was used in all subsequent syntheses.

TABLE 2.2 FUNCTIONALISED POLYSILOXANES. $Me_3SiO[Me_2SiO]_x[MeSi(R)O]_ySiMe_3$

Average	x	y	D.P.	mol%	L
(6a)	47	1	50	2	$(CH_2)_3NH(CH_2)_2NH_2$
(6b)	46	2	50	4	$(CH_2)_2NH(CH_2)_2NH_2$
(6c)	43	5	50	10	$(CH_2)_3NH(CH_2)_2NH_2$
(6d)	94	4	100	4	$(CH_2)_3NH(CH_2)_2NH_2$
(7a)	47	1	50	2	$CH=CH_2$
(7b)	46	2	50	4	$CH=CH_2$
(7c)	43	5	50	10	$CH=CH_2$
(8a)	3	5	10	50	$(CH_2)_4CH=CH_2$
(8b)	46	2	50	4	$(CH_2)_4CH=CH_2$
(9a)	3	5	10	50	$(CH_2)_2C_6H_9$
(9b)	46	2	50	4	$(CH_2)_2C_6H_9$
(9c)	43	5	50	10	$(CH_2)_2C_6H_9$
(10a)	3	5	10	50	$(CH_2)_3C_6H_5$
(10b)	46	2	50	4	$(CH_2)_3C_6H_5$
(11a)	46	2	50	4	$(CH_2)_2SCH_2COOH$
(11b)	43	5	50	10	$(CH_2)_2SCH_2COOH$
(12a)	46	2	50	4	$(CH_2)_3SH$
(12b)	43	5	50	10	$(CH_2)_3SH$
(13a)	46	2	50	4	H
(13b)	190	8	200	4	H
(14a)	46	2	50	4	$(CH_2)_2PPh_2$
(14b)	43	5	50	10	$(CH_2)_2PPh_2$
(15a)	46	2	50	4	$(CH_2)_2SPh$
(15b)	43	5	50	10	$(CH_2)_2SPh$
(16)	46	2	50	4	$(CH_2)_2SBu$
(17)	46	2	50	4	$(CH_2)_6PPh_2$
(18)	46	2	50	4	$(CH_2)_6SPh$

	Average x	y	D.P.	mol%	L
(19)	46	2	50	4	$(CH_2)_2Br$
(20)	46	2	50	4	$(CH_2)_2I$
(21)	46	2	50	4	$\{(CH_2)_3\overset{+}{N}HEt(CH_2)_2\overset{+}{N}H_2Et\}2Br^-$
(22)	43	5	50	10	$(CH_2)_3SEt$

The $-(CH_2)_3NH(CH_2)_2NH_2$ functionalised polysiloxanes (6a-d) were prepared by an <u>in situ</u> hydrolysis/condensation equilibration process which was originated in the laboratories at Dow Corning Ltd (equation 66)

$$(MeO)_2MeSi(CH_2)_3NH(CH_2)_2NH_2 + HO[Me_2SiO]_nH + Me_3SiO[Me_2SiO]_2SiMe_3$$

$$\downarrow \text{ 40\% aqueous KOH}$$

$$Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2CH_2NHCH_2CH_2CH_2NH_2)O]_2SiMe_3 \qquad (66)$$

$$+ MeOH + H_2O$$

Initial reactions in the synthesis are

(1) hydrolysis of N-(2-aminoethyl)-3-aminopropyldimethoxymethylsilane (I), so eliminating methanol (equation 67),

$$(MeO)_2SiMe(CH_2)_3NH(CH_2)_2NH_2 + H_2O$$

(I)

$$\rightarrow (HO)(MeO)SiMe(CH_2)_3NH(CH_2)_2NH_2 + MeOH \qquad (67)$$

(2) condensation of (I) with $HO[Me_2SiO]_nH$ (II), and

(3) condensation of

(i) (II) with itself (equation 68)

(ii) the hydrolysate of (I) with itself or (I) (equation 69).

$$\equiv SiOH + \equiv SiOH \rightarrow \equiv SiOSi\equiv + H_2O \quad (68)$$

$$\equiv SiOH + \equiv SiOMe \rightarrow \equiv SiOSi\equiv + MeOH \quad (69)$$

Secondary reactions in the synthesis involve polymerisation and equilibration.

Many problems were found in the original synthetic procedure (Experimental - Method (1)) used by Dow Corning Limited in the manufacture of this polymer. Even when preparations were carried out under what appeared to be identical conditions, the products were shown to have varying molecular weights and viscosities (Table 2.3). In addition, the products appeared to be unstable, as indicated by the formation of a slight haze which developed over a two month period, and a highly insoluble material which was deposited during the course of the synthesis. In the preparation of this polymer the starting materials, the catalyst (aqueous potassium hydroxide) and water were carefully heated to 140°C (avoiding 'frothing' of the reactant mixture and subsequent 'boil over'). Volatiles which formed (water and methanol and low molecular weight siloxanes) were allowed to distil over during the course of the reaction. The catalyst was finally deactivated by precipitation with sodium hydrogen carbonate. Following exhaustive investigations on Method (1), the variables found to affect the reproducibility were shown to be:

(1) the amount of water present at the start of the reaction,

(2) the rate of heating from room temperature to 140°C,

(3) the rate of agitation of the reaction mixture, and

(4) the rate of cooling of the product.

Following consultations with polymer chemists at Dow Corning Ltd., it was suggested that the poor reproducibility of the method could be attributed to the loss of catalyst (KOH) during equilibration, due to the formation of insoluble deposits of potassium silicates and silanolates. Attempts were therefore made to monitor the potassium content of amine functionalised polymers via atomic absorption spectroscopy. The results

TABLE 2.3 POTASSIUM CONCENTRATIONS FOR SELECTED AMINE FUNCTIONALISED POLYSILOXANES

mol%	Viscosity (cS)	[K]ppm
2	148	36
2	247	284
2	195	178
2	86	0
2	92	0
4	8	0
10	141	2

(Table 2.3) showed that the lower viscosity fluids, which were comparatively stable, contained low or zero concentrations of potassium, whereas the more viscous fluids contained 200 - 400 ppm of potassium. It was therefore concluded that the added sodium

hydrogen carbonate was not always effective in precipitating potassium ions, which ended up contaminating the polymers. In addition, fluids with high potassium concentrations, (and hence containing residual KOSi≡) showed a signal in their ^{1}H-nmr spectra at ca. 7.2ppm, caused by the base catalysed H-D exchange reaction between the amine protons of the polymer and the deuterated chloroform used as solvent.

The following revisions were made to method (1):

(1) The water:silane ratio was reduced from 5:1 to 1.1:1. This resulted in less 'foaming' in the work-up of the reaction mixture and hence facilitated this procedure.

(2) The neutralisation was carried out with acetic acid, and the neutralisation conditions were changed to four hours agitation at room temperature.

This method, designated method (2), yielded far more reproducible polymers which did not develop a haze and maintained constant viscosities and molecular weights over several months. Potassium concentrations in the $-(CH_2)_3NH(CH_2)_2NH_2$ functionalised polysiloxanes derived via method (2) were found to be very low (0-10ppm).

Polysiloxanes with $-CH=CH_2$ and $-(CH_2)_2SCH_2COOH$ functionalities were prepared in single stage processes (equation 70).

$$x[Me_2SiO]_4 + y[MeSi(R)O]_4 + n(Me_3Si)_2O$$

$$\xrightarrow[\text{TFMSA}]{140^{o}C} nMe_3SiO[Me_2SiO]_{4x}[MeSi(R)O]_{4y}SiMe_3 \qquad (70)$$

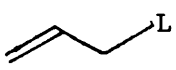
'EQUILIBRATE' (where R = $-CH=CH_2$ or $-(CH_2)_2SCH_2COOH$)

The method involves the equilibration of the starting materials employing TFMSA as catalyst, followed by subsequent neutralisation and stripping of volatiles.

The use of platinum group metal catalysts to promote the addition of ≡Si-H to olefinic double bonds (equation 71) is well established[161], and has been shown by Speir et al to be a very

$$\equiv SiH + C=C \xrightarrow{'Pt'} \equiv Si-C-C-H \qquad (71)$$

general reaction applicable to a wide range of substrates[162,163]. This procedure has proved very useful for modifying the decasiloxane $Me_3SiO[Me_2SiO]_3[MeSi(H)O]_5SiMe_3$ prior to polymerisation. Addition of this decasiloxane to allylbenzene, 4-vinylcyclohexene and hexa-1,5-diene has been carried out (equation 72) resulting in complete alkylation of all ≡SiH moieties.

$$Me_3SiO[Me_2SiO]_3[MeSi(H)O]_5SiMe_3 + \text{  }$$

$$\xrightarrow{'Pt'} Me_3SiO[Me_2SiO]_3[MeSi(CH_2CH_2L)O]_5SiMe_3 \qquad (72)$$

(L = C_6H_9, $-CH_2C_6H_5$ or $-(CH_2)_2CH=CH_2$)

In the preparation of polymer (8a) and (9a), a large excess of hexa-1,5-diene or 4-vinylcyclohexene was employed to avoid saturation of the second double bond in the substrate. Both infrared and ^{1}H-nmr spectral data confirmed that the reaction had proceeded as desired.

It was found necessary to use the low molecular weight precursors (8a), (9a), and (10a) for the preparation of the functionalised materials (8b), (9b-c) and (10b-c) as attempts to produce these polymers directly in the presence of a platinum catalyst resulted in considerable cross-linking and the formation of highly viscous products. Thus, the low molecular weight precursors were equilibrated with $[Me_2SiO]_4$ and $(Me_3Si)_2O$ (equation 73), employing trifluoromethanesulphonic acid as catalyst, in order to produce the high molecular weight polymers (8b), (9b-c) and (10b-c).

$$4Me_3SiO[Me_2SiO]_3[MeSi(R)O]_5SiMe_3 + 112[Me_2SiO]_4 + 6(Me_3Si)_2O \xrightarrow{\text{TFMSA}} 10Me_3SiO[Me_2SiO]_{46}[MeSi(R)O]_2SiMe_3 \quad (73)$$

(R = $-CH_2CH_2C_6H_{11}$, $-CH_2CH_2CH_2C_6H_5$, $-CH_2CH_2CH_2CH_2CH=CH_2$)

The polymers produced by this method were very slightly discoloured due to the presence of very small traces of residual platinum. In any subsequent reactions in which these polymers have been used as catalyst supports, the catalytic activity of the corresponding

unmetallated polymer containing residual platinum was first evaluated, and in all cases found to be zero.

Polysiloxanes with the $-CH_2CH_2CH_2SH$ functionality (12a-b) have been synthesised in a two-step procedure involving hydrolysis (equation 74) and equilibration (equation 75).

$$(MeO)_2MeSi(CH_2)_3SH + H_2O \xrightarrow[\text{hydrolysis}]{HCl} [MeSi(CH_2CH_2CH_2SH)O]_M + MeOH \qquad (74)$$

$$[Me_2SiO]_n + [MeSi(CH_2CH_2CH_2SH)O]_M + (Me_3Si)_2O \xrightarrow[\text{'equilibration'}]{TFMSA} Me_3SiO[Me_2SiO]_n[MeSi(CH_2CH_2CH_2SH)O]_MSiMe_3 \qquad (75)$$

The phosphino and alkyl- and arylthio functionalised polysiloxanes (14) - (18) were prepared in quantitative yields by an identical photochemical procedure to that used for the syntheses of the functionalised trisiloxanes (3), (4) and (5). All phosphine functionalised polysiloxanes were obtained as clear transparent fluids when hot, but on cooling they tended to deposit small amounts of a white precipitate, with the solution itself becoming slightly hazy. On warming, the products became homogeneous again. It appears that the precipitates either result from the formation of traces of a phosphine oxide produced during the photochemical reaction (some molecular oxygen may have been retained within the siloxane framework although the starting materials were thoroughly degassed), or, more likely, are incompatible polymer fractions containing differing proportions of phosphorus, possibly arising from incomplete equilibration.

The phosphine functionalised polysiloxane (14b) has also been prepared by the free radical catalysed addition of $HPPh_2$ to the appropriate vinyl functionalised substrate, using 2,2'-azobis(2-methylpropionitrile) (AZBN). Due to the convenience of the photochemical route, this latter procedure has not been employed extensively.

2.2.3. MISCELLANEOUS AND FAILED REACTIONS

2.2.3.a. Quaternisation of(6b)

A quaternised amine functionalised polysiloxane was considered useful for binding anionic catalytic species such as $PdCl_4^{2-}$ and $PtCl_4^{2-}$, and attempts were therefore made to prepare such a polymer from a $-NHCH_2CH_2NH_2$ containing precursor. A quantitative reaction occurred between HCl gas and (6b) dissolved in toluene, so yielding a highly viscous gel on removal of solvent in vacuo. As the polymer backbone is somewhat acid sensitive, it is possible that polymer breakdown occurred and hence alkyl halide were subsequently used as quaternising agents. The compound (6b) in acetone, reacted on stirring with bromoethane in the absence of light to yield the quaternised polymer, which appeared to be unstable and was shown spectroscopically to contain impurities due to partial decomposition. Consequently no further studies or metallations have been carried out on this material.

2.2.3.b. Attempted Preparation of

$$Me_3SiO[Me_2SiO]_x[MeSi(CH_2CH_2CH_2PPh_2)O]_ySiMe_3$$

All attempts to synthesise this material by photochemical or free radical catalysed procedures were unsuccessful.

1) Photochemically.

No significant reaction occurred on prolonged u.v. irradiation of a mixture of $Me_3SiO[Me_2SiO]_3[MeSi(H)O]_5SiMe_3$ and allyldiphenylphosphine.

2) Free Radical Route.

(i) Using AZBN. This method is analogous to that successfully used in the preparation of previous phosphine functionalised polysiloxanes, but could not be applied successfully for the analogue with a three-carbon spacer arm.

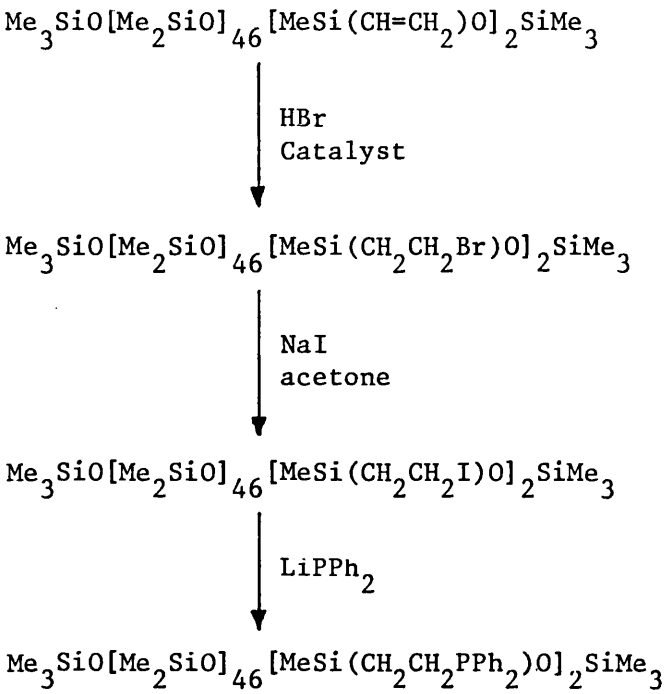
(ii) Using free radicals derived from benzophenone. Substitution reactions initiated by sodium diphenylketyl have been described[164], but $[Ph_2CO]^{\bullet}$ in THF failed to initiate the reaction between $Me_3SiO[Me_2SiO]_3[MeSi(H)O]_5SiMe_3$ and allyldiphenylphosphine.

2.2.3.c. Attempted Preparation of (14a)

It has been reported in the literature[86] that phosphine functionalised polysiloxanes may be prepared by the direct reaction of $LiPPh_2$ with a $-CH_2CH_2I$ functionalised polysiloxane (Scheme 17). Attempts were made to repeat this procedure.

The first stage in the synthesis involved the preparation of a 2-bromoethyl functionalised polysiloxane. Benzoyl peroxide was used as catalyst to give regiospecific addition of HBr across the vinyl functionality. The second step involved halide substitution[165] and in the final stage attempts were made to cleave the CH_2-I linkage and form a $-H_2C-PPh_2$ moiety.

Scheme 17



This procedure was carried out exactly as described by Farrel et al[86] but in our hands the final stage of the reaction inevitably resulted in Si-O bond cleavage and degradation of the siloxane backbone, as well as introduction of the $-PPh_2$ moiety, as indicated by both infrared and ^{1}H-nmr spectroscopy. Interestingly, no such degradation is mentioned in reference 86.

2.3. EXPERIMENTAL

2.3.1. SYNTHESIS OF MODEL SILOXANES

$Me_3SiO[MeSi(H)O]SiMe_3$ (1)

A mixture of $Me_3SiO[MeSi(H)O]_nSiMe_3$ (n≃40) (25.6g, 10.0mmol) $(Me_3SiO)_2O$ (75.7g, 0.39mol), TFMSA (0.10% ^{v}/w, 0.10g, 0.67mmol) and H_2O (0.01% ^{v}/w, 0.01g, 0.56mmol) were equilibrated at 60 - 65^{o}C under a dinitrogen atmosphere for 3h. DMF (0.05g) was added and

the solution was stirred for 1h. at 60°C. The solution was then cooled to <25°C and filtered after addition of dicalite. The filtrate was then distilled at 760mmHg, and the following fractions collected.

TABLE 2.4 PHYSICAL DATA FOR $Me_3SiO[MeSi(H)O]_nSiMe_3$

Fraction	Yield(%)	B.P.(°C)	Distillate
1	15	90-139°C	$(Me_3Si)_2O$, Me_3SiOH
2	51	139-144°C	$(Me_3SiO)_2Si(Me)H$ (1)
Residue	22	>144°C	$Me_3SiO[MeSi(H)O]_nSiMe_3$ (n>1)

Compound (1) was obtained as a colourless fluid (found: C, 37.8; H, 9.85. $C_7H_{22}O_2Si_3$ requires C, 37.8; H, 9.91%).

$Me_3SiO[MeSi(CH=CH_2)O]_nSiMe_3$ (n = 1, 2 and 3) (2) (a)-(c)

A solution containing dichloromethylvinylsilane, $SiMeCl_2(CH=CH_2)$ (13.1g, 93.2mmol) and trichloromethylsilane $SiMe_3Cl$ (20.2g, 186.4mmol) in diethyl ether (25cm^3) was added dropwise with stirring to water (20cm^3) cooled in ice. The mixture was allowed to warm with stirring to ambient temperature over 1h. The ether layer was separated, dried using magnesium sulphate, filtered and the solvent removed in vacuo. Distillation of the residual oil under reduced pressure yielded the tabulated compounds(Table 2.5), higher siloxanes remaining undistilled.

TABLE 2.5 PHYSICAL AND ANALYTICAL DATA FOR

$Me_3SiO[MeSi(CH=CH_2)O]_nSiMe_3$ (n = 1, 2 and 3)

Compound	Yield (%)	B.P.(°C)	P/mmHg	Analysis[a](%)	
				C	H
(2a) n = 1	16	41	1.5	43.6(43.5)	9.40(9.65)
(2b) n = 2	44	68	1.5	b	
(2c) n = 3	24	85	1.5	b	

[a] Calculated data in parentheses

[b] Not characterised further

$Me_3SiO[MeSi(CH_2CH_2PPh_2)O]SiMe_3$ (3)

Stoichiometric amounts of (2) (2.48g, 0.01mol) and diphenylphosphine (1.86g, 0.01mol) were stirred, in the absence of solvent, in a sealed tube under a dinitrogen atmosphere while irradiated with ultraviolet light from a 400W lamp for 48h. The air-sensitive product was distilled under reduced pressure and was isolated as a colourless oil. (3.60g, 83%) b.p. 171°C (0.8mmHg). (Found: C, 58.5; H, 7.95. $C_{21}H_{35}O_2PSi_3$ requires C, 58.1, H, 8.05%).

$Me_3SiO[MeSi(CH_2CH_2SPh)O]SiMe_3$ (4)

Stoichiometric amounts of (2) (2.48g, 0.01mol) and thiophenol (1.10g, 0.01mol) were irradiated with ultraviolet light in an identical manner to that above. The product was obtained in

qualitative yield as a foul smelling mobile yellow fluid, which appeared spectroscopically and analytically pure without further treatment. (Found: C, 50.1; H, 8.32. $C_{15}H_{30}O_2SSi_3$ requires C, 50.3; H, 8.38%).

$Me_3SiO[MeSi(CH_2CH_2SBu)O]SiMe_3$ (5)

A mixture of (2) (2.48g, 0.01mol) and 1-butanethiol (0.90g, 0.01mmol) was irradiated with ultraviolet light in an analogous manner to that given above for (3). The product was obtained as a foul smelling mobile yellow fluid which was not purified further, but appeared analytically and spectroscopically pure as prepared. (Found: C, 46.1%; H, 9.84%. $C_{13}H_{34}O_2SSi_3$ requires C, 46.2%; H, 10.06%).

2.3.2. SYNTHESIS OF POLYSILOXANES

For each polymer, the qualifiers a, b and c refer to different mol% and/or different degrees of polymerisation (D.P.). In this section, only the syntheses of the low molecular weight precursors (8a), (9a), (10a) and all the 50D.P. 4mol% polymers have been described. Other polymers were obtained by analogous procedures using appropriate ratios of starting materials.

$Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2CH_2NHCH_2CH_2NH_2)O]_2SiMe_3$ (6b)

Method 1: A mixture of $H[Me_2SiO]_{48}OH$ (203.5g, 57.0mmol), $Me_3SiO[Me_2SiO]_2SiMe_3$ (19.3g, 0.062mol), $(MeO)_2MeSi(CH_2)_3NH(CH_2)_2NH_2$ (25.8g, 0.13mol), H_2O (56.0g, 3.0mol) and a solution of 40%^{w}/w aqueous potassium hydroxide (present as 0.38% ^{w}/w of the total charge of the reaction mixture i.e. 0.99g) were heated in an

atmosphere of nitrogen from room temperature to 145°C and held at 145 - 155°C for five hours. During the initial stages of the heating-up period, volatiles (mainly methanol and water) distilled from the reaction vessel (ca. 30g). Extreme care had to be taken throughout the preparation as the reaction mixture was prone to 'frothing'. The crude $-(CH_2)_3NH(CH_2)_2NH_2$ functionalised polymeric product (222g) was then stirred vigorously at 60 - 80°C for 1h. in an atmosphere of N_2 gas with sodium hydrogen carbonate (0.91g, 10.9mmol, 0.35% $^w/_w$ of the polymer charge). The polymer was stripped of further volatile components in the presence of the inorganic salts until a temperature and pressure of 155°C and 50mmHg respectively were reached. These conditions were maintained for 2h. by which time 12g of volatiles had been collected. The polymer was then cooled to <30°C and filtered twice using dicalite, so yielding the product (216g) as a mobile, clear, yellow fluid.

Method 2: The overall reaction was carried out in a similar manner to that described above in method (1), but with the following improvements:

(1) the mole ratio of water to silane was lowered from ca. 5:1 to 1.1:1 (i.e. using 11.2g, 0.62mol of water),

(2) investigations carried out by Dow Corning Ltd. had shown acetic acid to be more effective than $NaHCO_3$ as a "neutralising" agent, and 1.5moles of acetic acid per 39g of potassium salt was used to neutralise the KOH catalyst,

(3) the neutralisation reaction conditions were changed to 3-4h. agitation at room temperature.

Using Method (2) polysiloxanes (6b-e) were prepared in a similar way by varying the ratios of the starting materials as appropriate. For 6(b) Found: C, 34.0; H, 8.41; N, 1.50. $C_{110}H_{326}N_4O_{49}Si_{50}$ requires C, 34.0; H, 8.39; N, 1.44%). Viscosity 86cS.

$Me_3SiO[Me_2SiO]_{46}[MeSi(CH=CH_2)O]_2SiMe_3$ (7b)

A mixture of $[MeSi(CH=CH_2)O]_4$ (8.6g, 25mmol), $[Me_2SiO]_4$ (166.5g, 0.56mol) and $Me_3SiO[Me_2SiO]SiMe_3$ (11.8g, 0.05mol) were equilibrated under a nitrogen atmosphere at 130°C employing TFMSA (0.187g, 1.25mmol, ≃0.1% on total charge) as catalyst. Water (0.18g, 0.01mol) was also added to activate the catalyst. After 4h. equilibration was complete. DMF (0.94g) was added to neutralise the acid catalyst and the mixture was then agitated at 60-70°C for 1h. The polymer was cooled to room temperature and filtered with dicalite as a filter-aid. The filtrate was then stripped of volatiles (13g) at 145°C and 10mmHg for 2h., so generating the vinyl functionalised polymer (147g) as a mobile homogeneous and colourless fluid. (Found: C, 33.0; H, 8.22. $C_{104}H_{306}O_{49}Si_{50}$ requires C, 33.4; H, 8.19%). Viscosity 98cS.

$Me_3SiO[Me_2SiO]_3[MeSi(CH_2CH_2CH_2CH_2CH=CH_2)O]_5SiMe_3$ (8a)

A solution of hexa-1,5-diene (32.8g, 0.4mol) and a 10% $^w/_v$ solution of $H_2PtCl_6.6H_2O$ in isopropyl alcohol (0.005cm^3, 0.01mol) was heated under N_2 to 50°C in a 250ml flask equipped with a stirrer, thermocouple, condenser dropping funnel. $Me_3SiO[Me_2SiO]_3[MeSi(H)O]_5SiMe_3$ (13.7g, 0.1mol ≡SiH) was added dropwise over a 45 minute period. The reactants were stirred at 55°C for a further 6h., by which time infrared spectroscopy indicated the complete loss of ≡Si-H

(ν = 2150cm^{-1}). Volatiles were distilled from the product at 120°C and 50mmHg pressure, so leaving the polymer (20g) as a colourless mobile fluid (Found: C, 50.8; H, 9.60. $C_{47}H_{106}O_9Si_{10}$ requires C, 51.6; H, 9.69%).

$Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2CH_2CH_2CH=CH_2)O]_2SiMe_3$ (8b)

A mixture of (8a) (21.9g, 20.0mmol), $[Me_2SiO]_4$ (165.8g, 0.56mol) and $(Me_3Si)_2O$ (4.85g, 30.0mmol) was heated to 40°C. TFMSA (0.21g, 0.13 cm^3, 40mmol) and water (0.02ml) were added. The mixture was stirred and warmed to 70°C under a N_2 atmosphere, by which time the fluid had turned to a faint brown-black. After 4h., viscosity measurements indicated the equilibration reaction to be complete. The catalyst was neutralised by addition of DMF (0.10g.) and the mixture stirred at 70°C for 1h., during which time the catalyst decomposed and precipitated as a black colloidal suspension. The fluid was allowed to cool to ambient temperature and the product filtered twice in the presence of dicalite filter aid. The volatile compounds present (18g), were then removed by distillation under vacuum (10mmHg) at 120°C and the polymer held at this temperature for two hours. Dicalite was again added and the fluid filtered, so leaving the product (163g) as a homogeneous clear, mobile fluid with a very faint brown discoloration. (Found: C, 35.2; H, 8.42. $C_{112}H_{322}O_{49}Si_{50}$ requires C, 34.9; H, 8.36%). Viscosity 129cS.

$Me_3SiO[Me_2SiO]_3[MeSi(CH_2CH_2C_6H_9)O]_5SiMe_3$ (9a)

This polymer was synthesised by a similar procedure to that used for (8a). 4-Vinylcyclohexene (432g, 4mol) and a 10% $^w/_v$ solution of $H_2PtCl_6.6H_2O$ in isopropyl alcohol (0.104cm^3, 0.2 x 10^{-4}mol) were heated to 80°C. The isomantle was removed and

$Me_3SiO[Me_2SiO]_3[MeSi(H)O]_5SiMe_3$ (274g, 2mol SiH) was slowly added aiming at a rate such that the exothermic reaction that ensued maintained the reaction mixture at a temperature of 100 - 110°C. When all of the SiH compound had been added (approximately 0.5h) the reactants were stirred for a further 3h. until infrared spectroscopy revealed complete loss of ≡SiH (ν = 2150cm^{-1}). The volatile compounds present were then distilled at 80mmHg and 120°C, leaving a clear mobile fluid (370g) (Found: C, 54.3; H, 9.40. $C_{57}H_{116}O_9Si_{10}$ requires C, 55.9; H, 9.48%).

$Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2C_6H_9)O]_2SiMe_3$ (9b)

A mixture of (9a) (24.5g, 20.0mmol), $[Me_2SiO]_4$ (165.8g, 0.56mol), $(Me_3Si)_2O$ (4.85g, 30.0mmol) were polymerised, equilibrated, neutralised and stripped in an identical manner to that described above for (8b). The polymer was again obtained as a clear mobile homogeneous fluid with a very slight yellow coloration. (Found: C, 36.2; H, 8.21. $C_{116}H_{326}O_{49}Si_{50}$ requires C, 35.7; H, 8.35%). Viscosity 85cS.

$Me_3SiO[Me_2SiO]_3[MeSi(CH_2CH_2CH_2C_6H_5)O]_5SiMe_3$ (10a)

The above compound was obtained using a similar procedure to that for (8a) and (9a) above. Allylbenzene (25.96g, 0.11mol) and a 10% $^w/_v$ solution of $H_2PtCl_6.6H_2O$ in IPA (0.005cm^3, 0.01mol) were heated to 80°C. The compound $Me_3SiO[Me_2SiO]_3[MeSi(H)O]_5SiMe_3$ (13.74g, 0.10mol SiH) was added dropwise and the reactants held at 120°C for 4h. A colourless mobile fluid (28.0g) was obtained, following the normal work-up procedure. (Found: C, 58.2; H, 8.61. $C_{62}H_{106}O_9Si_{10}$ requires C, 58.4; H, 8.32%).

$Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2CH_2C_6H_5)O]_2SiMe_3$ (10b)

A mixture of (10a) (25.4g, 20.0mmol), $[Me_2SiO]_4$ (165.8g, 0.56mol), and $(Me_3Si)_2O$ (3.9g, 2.4mmol) were treated in an identical manner to that for (8b). The clear and mobile fluid obtained had a very faint brown discoloration. (Found: C, 36.4; H, 8.52. $C_{118}H_{322}O_{49}Si_{50}$ requires C, 36.1; H, 8.21%). Viscosity 118cS.

$Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2SCH_2COOH)O]_2SiMe_3$ (11a)

A mixture of $[MeSi(CH_2CH_2SCH_2COOH)O]_4$ (8.9g, 25.0mmol) $(Me_2SiO)_4$ (166.5g, 0.56mol) and $(Me_3Si)_2O$ (11.8g, 0.05mol) were heated to 70 - 80°C (until miscible), before addition of TFMSA (0.19g, 1.3mmol) and water (0.20g, 11.1mmol) as catalyst. The mixture was then held at 80°C for 3h. until viscosity measurements became constant. At this stage DMF (0.95g) was added to neutralise the reaction mixture which was subsequently further agitated at 70°C for 1h. under nitrogen. The crude polymer was cooled to <30°C and then filtered employing dicalite as a filter-aid. The polymer was stripped to 145°C at 10mmHg pressure, and held at this temperature for 2h. The product was obtained as a homogeneous and highly viscous clear fluid. (Found: C, 33.5; H, 8.26; $C_{108}H_{314}O_{53}S_2Si_{50}$ requires C, 33.0; H, 8.01%) Viscosity 627cS.

$Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2CH_2SH)O]_2SiMe_3$ (12a)

The preparation of (12a) involves a two-step procedure. Step 1: To $(MeO)_2MeSi(CH_2)_3SH$ (93g, 0.51mol) and water (9.3g, 0.52mol), 2% aqueous hydrochloric acid solution (0.6g) was added dropwise as a highly exothermic reaction took place. The mixture was heated to reflux and volatiles (water and methanol) (18g) were distilled from the reaction vessel at 120°C and

atmospheric pressure. Toluene (20g, 20% based on the reactant charge) was added and the remaining water was collected azeotropically and any residual toluene was then stripped out to 120°C at 10mmHg pressure. The mixture was then treated for 1h. at 70°C with an excess of $NaHCO_3$ (5g, 0.06mol). The $-CH_2CH_2CH_2SH$ functionalised polysiloxane was allowed to cool and was then filtered twice in the presence of dicalite.

Step 2: The polymer $[MeSi(CH_2CH_2CH_2SH)O]_n$ (6.7g, 0.05 units) as prepared, $(Me_2SiO)_4$ (81g, 0.27mol) and $Me_3SiO[Me_2SiO]_2SiMe_3$ (7.75g, 0.025mol) were agitated in a three-necked flask equipped with a reflux condenser, a nitrogen inlet and thermocouple. The mixture was heated to 70°C (the mixture being heterogeneous at this stage). TFMSA (0.09g, 0.64mmol) was added as catalyst and the reaction mixture was held at 70 - 80°C under N_2 gas for 4h. The mixture became homogeneous in approximately 1h. at which stage DMF (0.045g) was added to neutralise the acid. Following further vigorous stirring at 70°C under nitrogen, the polymer was cooled to <25°C, stirred with dicalite for a further 2h. and then filtered. A colourless and clear homogeneous fluid (57.3g) was obtained. (Found: C, 31.3; H, 8.01. $C_{106}H_{314}O_{49}S_2Si_{50}$ requires C, 33.2; H, 8.19%) Viscosity 110cS.

$Me_3SiO[Me_2SiO]_{46}[MeSi(H)O]_2SiMe_3$ (13a)

A mixture of $Me_3SiO[Me_2SiO]_3[MeSi(H)O]_5SiMe_3$ (13.7g, 20.0mmol), $[Me_2SiO]_4$ (165.8g, 0.56mol) and $(Me_3Si)_2O$ (4.85g, 30.0mmol) were equilibrated and treated by a similar procedure to that described for (8b). Removal of volatiles from the reaction mixture left the required product as a colourless mobile fluid (161g). (Found:

C, 32.5; H, 8.12. $C_{100}H_{302}O_{49}Si_{50}$ requires C, 32.6; H, 8.19%). Viscosity 76cS.

$Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2PPh_2)O]_2SiMe_3$ (14a)

In an identical photochemical procedure to that for (3), stoichiometric amounts of (7b) (3.74g, 1.0mmol) and diphenylphosphine (0.372g, 2.0mmol) were irradiated with ultraviolet light for 48h. in the absence of solvent. The polymer was obtained as an air sensitive, hazy fluid. A small quantity of white precipitate deposited on cooling the product. This solid appeared analytically and spectroscopically identical to the polymer fluid, and it could be redissolved in the fluid on warming, so yielding a clear homogeneous liquid. (Found: C, 36.2; H, 7.80. $C_{128}H_{328}O_{49}P_2Si_{50}$ requires C, 37.4; H, 7.98%).

$Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2PPh_2)O]_2SiMe_3$ (14a)

In an alternative method to that given above, (7b) (7.48g, 2mmol), toluene (25ml) and 2,2'-azobis-(2-methylpropionitrile) present as 0.1%^{v}/w were warmed under a nitrogen atmosphere to 70 - 80^{o}C. Diphenylphosphine (0.75g, 4.0mmol) was added dropwise via a syringe. The reactants were held at this temperature for 4h. and infrared spectroscopy was used to monitor the disappearance of the P-H stretch at 2250cm^{-1} as the reaction proceeded. Toluene was then slowly distilled off at 125^{o}C and 0.1mmHg pressure, and the catalyst also sublimed out at this temperature and finally removed completely with the aid of a hot air gun. The product was obtained as a hazy white, mobile fluid. (Found: C, 38.4; H, 7.85. $C_{128}H_{328}O_{49}P_2Si_{50}$ requires C, 37.4; H, 7.98%).

$Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2SPh)O]_2SiMe_3$ (15a)

A mixture of (7b) (3.74g, 1.00mmol) and thiophenol (0.22g, 2.0mmol) were irradiated with ultraviolet light in an analogous method to that given for (3), so producing a clear yellow mobile fluid, which was not purified further. (Found: C, 36.2; H, 8.16. $C_{116}H_{318}O_{49}S_2Si_{50}$ requires C, 35.2; H, 8.03%).

$Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2SBu)O]_2SiMe_3$ (16)

Irradiation of (7b) (3.74g, 1mmol) and 1-butanethiol (0.18g, 2.0mmol) with ultraviolet light as above for (15a) yielded a clear yellow fluid which appeared spectroscopically and analytically pure. (Found: C, 34.2; H, 8.43. $C_{112}H_{326}O_{49}S_2Si_{50}$ requires C, 34.3; H, 8.32%).

$Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2CH_2CH_2CH_2CH_2PPh_2)O]_2SiMe_3$ (17)

By using an identical procedure as that for above, the polymer was prepared as a hazy mobile fluid on irradiation of (8b) (3.85g, 1mmol) and diphenylphosphine (0.37g, 2.0mmol). No purification procedures were carried out. (Found: C, 38.0; H, 7.93. $C_{136}H_{344}O_{49}P_2Si_{50}$ requires C, 38.7; H, 8.15%).

$Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2CH_2CH_2CH_2CH_2SPh)O]_2SiMe_3$ (18)

The product was obtained as a clear yellow fluid on the u.v. irradiation of (8b) (3.85g, 1.0mmol) and thiophenol (0.22g, 2.0mmol). (Found: C, 34.8; H, 7.91. $C_{124}H_{334}O_{49}S_2Si_{50}$ requires C, 36.5; H, 8.19%).

$Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2Br)O]_2SiMe_3$ (19)

Anhydrous HBr was bubbled slowly for 1.5h. through (7b) (7.48g, 2mmol) in toluene (20ml) containing a catalytic quantity (0.10g) of benzoyl peroxide (infrared spectroscopy was used to monitor the disappearance of the vinyl absorption at $1600cm^{-1}$). The solvent was carefully removed in vacuo (avoiding 'frothing') and the product filtered yielding a clear, yellow, mobile unstable fluid. (Found: C, 30.3; H, 7.61; Br, 3.93. $Br_2C_{104}H_{308}O_{49}Si_{50}$ requires C, 32.0; H, 7.90; Br, 4.10%).

$Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2I)O]_2SiMe_3$ (20)

A solution of (19) (3.9g, 1mmol) in acetone ($15cm^3$) was heated under reflux in a nitrogen atmosphere with excess sodium iodide (0.45g, 3mmol) for 10 days. Complete halogen exchange was confirmed by ^{1}H-NMR spectroscopy, following filtration and evaporation of the solvent.

2.3.3. Miscellaneous Reactions

$[Me_3SiO\{Me_2SiO\}_{46}\{MeSi(CH_2CH_2CH_2\overset{+}{N}(C_2H_5)HCH_2CH_2\overset{+}{N}(C_2H_5)H_2)O\}_2SiMe_3]4Br^-$ (21)

Quaternisation of (6b) was achieved by reaction with excess bromoethane in acetone. The reactants were stirred for 12 hours in acetone in the absence of light. Removal of the solvent, and further washings with acetone followed by subsequent removal of solvent yielded a reddish unstable fluid. Analytical data for C, H, N and Br were in reasonable agreement for the fully quaternised polymer. (Found: C, 34.6; H, 8.52; N, 1.35; Br, 7.13% Calculated: C, 32.8; H, 8.01; N, 1.30; Br, 7.40%).

Attempted Preparation of $Me_3SiO[Me_2SiO]_{43}[MeSi(CH_2CH_2CH_2SEt)O]_5SiMe_3$ (22)

To (12b) (2.0g, 0.50mmol) in toluene ($10cm^3$) was added sodium hydroxide (0.27g) in water ($10cm^3$), together with an excess of bromoethane (0.55g, 5.0mmol) and a catalytic amount of benzyltriethylammonium chloride (0.02g). The mixture was vigorously shaken overnight at room temperature, and the organic layer was then separated, washed with water, dried over magnesium sulphate and the solvent removed *in vacuo* yielding a colourless mobile oil. ^1H nmr spectroscopy showed there to be definite differences between the starting material and the product indicating that some alkylation may have occurred, however, the quality of the spectra was poor and the reaction was not pursued further.

Attempted Preparation of $Me_3SiO[Me_2SiO]_3[MeSi(CH_2CH_2CH_2PPh_2)O]_5SiMe_3$

Benzophenone (91mg, 0.50mmol) was dissolved in THF ($20cm^3$) and finely cut sodium metal was added. The mixture was stirred for 2h. The resulting deep purple solution was assumed to be *ca.* 0.025mmol per cm^3 in $[Ph_2CO]^{\bullet}$. The polymer, $Me_3SiO[Me_2SiO]_3[MeSi(H)O]_5SiMe_3$ (13.68g, 20mmol) and allyldiphenylphosphine (22.6g, 0.1mol) were dissolved in THF ($10cm^3$), and the initiator solution added dropwise. There was an immediate colour change to light green (perhaps a concentration effect), but no obvious reaction occurred even on gradual warming to reflux temperatures (approximately 72^oC) and holding at this temperature for 48h.

Attempted Preparation of $Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2PPh_2)O]_2SiMe_3$ (14a)

Generation of the diphenylphosphine anion, PPh_2^- was achieved by the dropwise addition of n-BuLi (added as 0.187ml of a 1.55M hexane solution) to a solution of diphenylphosphine (0.186g, 1mmol) dissolved in THF ($5cm^3$) as 0^oC. The red solution so formed was stirred for 1h. and then treated dropwise with a solution of (20) (2.0g, 0.5mmol) dissolved in THF ($10cm^3$). The mixture was allowed to warm slowly to room temperature, at which stage a white precipitate formed which was later shown to be caused by breakdown of the polymer.

CHAPTER 3

IDENTIFICATION AND CHARACTERISATION OF FUNCTIONALISED ORGANOSILOXANES

3.1. SUMMARY.

The model functionalised organosiloxanes and polyorganosiloxanes whose syntheses are described in the preceding chapter, have been characterised by a combination of nuclear magnetic resonance, infrared spectroscopy and gel permeation chromatography. ^{1}H and ^{13}C-nmr data have been recorded routinely, and in the latter stages of this study, as high field ^{1}H and multinuclear facilities become available, ^{29}Si and some ^{31}P measurements were recorded on a selection of the polymers. Infrared spectroscopy has proved useful for monitoring the progress of reactions and for the qualitative confirmation of the presence of specific functional groups in the materials. Gel permeation chromatography has been used to monitor the purity and reproducibility of linear polymers and to evaluate their mean molecular weights.

3.2. NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

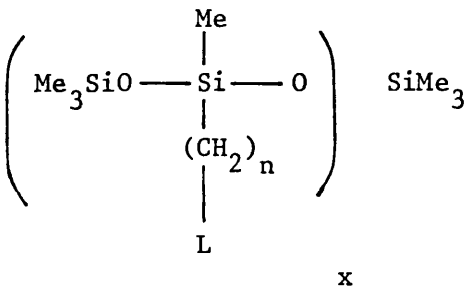
3.2.1. INTRODUCTION

All of the linear siloxanes synthesised in this study have excellent solubility in a large range of organic solvents, and as the resonances characteristic of the functional group present in the polymer are generally well separated from the Si-Me signals of the siloxane backbone, then ^{1}H-, ^{13}C- and ^{29}Si-nmr spectroscopies have proved extremely powerful tools in their identification and characterisation. Deuterochloroform was employed as solvent for all spectra described in this chapter, and spectra were recorded under an atmosphere of N_2 in degassed solvents for air sensitive compounds.

3.2.1.a ^{1}H- AND ^{13}C-NMR SPECTROSCOPIES

The use of ^{1}H- and ^{13}C-nmr spectroscopies in the characterisation of soluble carbon-functional silicon compounds is well established.[166] The relatively high sensitivity of ^{1}H-nmr makes it extremely useful for identification purposes, the chemical shifts providing information on the type and number of substituents in the methylene chain, and the splittings due to proton-proton couplings revealing structural relationships among various groups of protons. Two features of ^{13}C data are of particular value for studies of aliphatic carbon-functional siloxanes. These are the linear relationship between the carbon chemical shift, (δ) and the electron density at the carbon centre, and also the direct additivity of substituent effects.[167,168] The use of an INEPT[169] (insensitive nuclei enhancement polarisation transfer) sequence in ^{13}C-nmr measurements facilitates identification of the CH/CH_3 and CH_2 spectral resonances.

^{1}H- and ^{13}C-nmr data on a series of chlorosilanes have been reported previously,[83,160,162,163] and Brisdon and Watts[160] have listed spectroscopic data on a series of model organosiloxanes.



x

x = 1 or 2; L = -CN, $-PPh_2$, -halogen, -arene

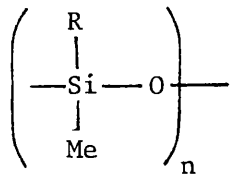
Based on these data the following generalised assignments can be made for the various methyl groups in both model siloxanes and polysiloxanes.

TABLE 3.1 ^{13}C-NMR CHEMICAL SHIFTS FOR Si-Me GROUPS

Type	Chemical shift (δ ppm rel. TMS)
Me_3SiO	2 ± 0.5
$Me\text{-}Si\text{-}(CH_2)_n\text{-}L$	0 ± 0.5

The ^{1}H- and ^{13}C-nmr spectra generally show well-resolved resonances for the $SiMe/SiMe_3$ moieties and the alkyl spacer chain of the functional group. For the latter, a methylene group bonded directly to silicon in general exhibits a shift of 13 - 16ppm (exceptionally over 20 ppm for a diphenylphosphine terminated chain). Methylene carbons β to the silicon atom have chemical shifts in the region of 20 - 30ppm.

Pelletier and Harrod[170] have recently used a simple empirical approach based on the chemical environment of the resonating protons to assign ^{1}H-nmr spectra and isomeric compositions of methylcyclosiloxanes of general structure:



n = 3, 4, or 5

R = CH_3, D_n

R = C_6H_5, D^{Ph}_n

R = Br, D^{Br}_n

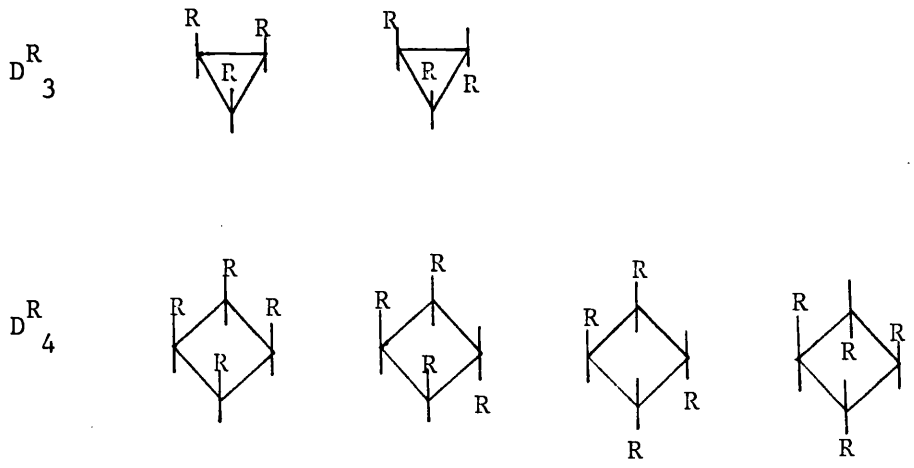
R = $Co(CO)_4$, D^{Co}_n

R = $Fe(CO)_2Cp$, D^{Fp}_n

R = H, D^{H}_n

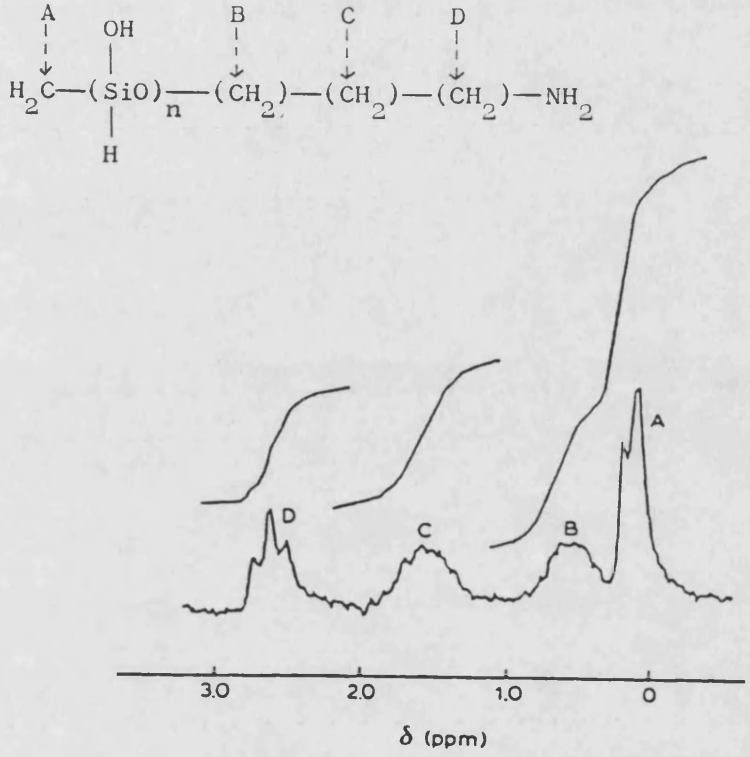
As prepared, cyclosiloxanes of a given ring size exist as a mixture of several isomeric forms as shown schematically in Figure 3.1 for D^R_3 and D^R_4 species.

FIGURE 3.1 SCHEMATIC REPRESENTATION OF GEOMETRIC ISOMERS OF D^R_n (n = 3 and 4)



The chemical shift of the methyl substituent was found to be dependent upon both size and, more strongly on the nature and orientation, of the neighbouring R groups. The authors reported that the ^{1}H-nmr spectra of methylhydridosiloxanes (D^{H}_{n}) exhibit resonances in the region 4.9 - 5.1ppm for Si-H protons and 0.1 - 0.2ppm for the methyl groups. Three-bond coupling between the hydrogen bonded to the silicon and the protons of the geminal methyl group was observed, with the Si-H region appearing as an unresolved cluster of overlapping bands. Similar coupling effects in the proton spectra of siloxanes, $Me_3SiO[MeSi(H)O]_nSiMe_3$ (n = 1, 2) have been reported by Watts[171], in which the Si-H proton resonance is again observed as an unresolved multiplet. Proton nmr data on the vinylsiloxane, $Me_3SiO[MeSi(CH=CH_2)O]SiMe_3$ have also been reported.[164,17] A maximum of 14 observable bands are expected for this ABC spin system[173], although only 10 are usually seen, and often the vinyl signal reduces to an apparent singlet because of accidental degeneracies[174] caused by the effect of electronegative substituents bound to silicon. In a further recent study, the proton nmr spectra of poly(cyanoethylmethylsiloxane) (PCEMS) and poly(aminopropylmethylsiloxane) (PAPMS) have been reported by Koyama *et al*[175]. The spectrum of PAPMS is poorly resolved but the following overall assignments were made (figure 3.2).

Figure 3.2



3.2.1b. ^{29}Si-NMR SPECTROSCOPY

^{29}Si is the only magnetically active natural isotope of silicon. It has spin I = ½ and a natural abundance of 4.70%. ^{29}Si chemical shifts cover a range of ca. 400ppm; most of the known shifts are, however, clustered in a narrower range of about 200ppm. This range is smaller than that for ^{13}C but nevertheless, the dispersion arising from structural effects is considerable, and ^{29}Si chemical shift measurements provide a valuable tool for the determination of molecular structure. For all ^{29}Si-nmr spectra recorded in this study, a shiftless relaxation agent, $Cr(acac)_3$, was added.

The effect of $Cr(acac)_3$ is two fold. Firstly, it quenches the nOe (Nuclear Overhauser Effect) which would result in the intensities of the signal being reduced or inverted[176]. Secondly, it reduces the spin-lattice relaxation times of the individual ^{29}Si nuclei to approximately the same value. These effects together allow semi-quantitative intensity measurements to be carried out. As multinuclear nmr facilities become more accessible, ^{29}Si-nmr is becoming increasingly important and this is reflected by increased coverage in many books.[166,177] Schraml[166] recently summarised the main features of ^{29}Si-nmr spectroscopy including experimental and theoretical aspects, chemical shift and spin-spin coupling data on a large number of carbon-functional organosilicon compounds. Harris et al[168] have tabulated chemical shift data for linear and cyclic siloxanes. The nomenclature used for polymethylsiloxane units is described below. The M, D notation refers to the number of oxygen atoms bonded to the silicon atom.

$Me_3SiO_{\frac{1}{2}}-$	$-O_{\frac{1}{2}}-Si(Me)_2-O_{\frac{1}{2}}-$
end units	chain units
M	D

Table 3.2 lists a selection of data for linear siloxane oligomers. Substitution of methyl groups is indicated by a superscript suffix, e.g. M^H implies the unit $HMe_2SiO_{\frac{1}{2}}-$.

TABLE 3.2 ^{29}Si CHEMICAL SHIFTS (δ_{Si}/ppm)[a] OF LINEAR SILOXANE OLIGOMERS[b] $M^{X}D^{Y}M_{n}$

X[c]	Y[c]	n = 1 M	n = 1 D	n = 2 M	n = 2 D
-	-	6.61	-21.46	6.78	-22.08
		6.70	-21.5	6.80	-22.0
-	H	8.72	-36.86	9.32	-36.41
-	Vi	d	-35.1		
-	Ph	7.2	-34.9		
-	Cl	9.8	-46.2		
-	OH	5.9	-57.1		
OMe	-	-12.5	-22.0	-12.0	-20.4
Ph_2	-	-12.5	-19.4		
Ph_2	Ph	-11.1	-32.4		
Ph_2	Ph_2	-10.5	-46.1		

[a] Adapted from ref. 168. [b] Excluding silicate ions and $M^{OH}D_nM^{OH}$. [c] All Me except where otherwise stated. [d] Not reported.

Harris et al have also listed chemical shift data for selected cyclic siloxanes (Table 3.3).

TABLE 3.3 ^{29}Si CHEMICAL SHIFTS (δ_{Si}/ppm)[a] FOR CYCLIC SILOXANES

X	D_3^X	D_4^X	D_5^X
Me	-9.2	-20.0	-22.8
H		-32.4 to -33.0	-34.4 to -34.9
Ph	-20.6 to -20.7	-30.1 to -30.4	-32.4 to -32.8
Vi		-32.6 to -32.8	

[a] Adapted from ref. 168

Levy et al[178] have determined ^{29}Si chemical shifts and spin-lattice relaxation times in low molecular weight linear polydimethylsiloxanes, $Me_3SiO[Me_2SiO]_nSiMe_3$, (MD_nM). In the ^{29}Si-nmr spectra of the oligomers MD_nM (n = 1 to 8), individual resonances were observed for each distinct silicon nucleus, the degree of chemical shift resolution being much greater than that for ^{13}C- and ^{1}H-nmr[179]. The high values determined for the spin-lattice relaxation times reveal the high mobility of the polymer chains. In a complementary study, Weber et al[180] have recently investigated both chemical shifts and spin-lattice relaxation times in the ^{29}Si-nmr spectra of polymethylhydridosiloxanes, $Me_3SiO[MeSi(H)O]_nSiMe_3$ (n = 3 to 8 and 35). Other examples of ^{29}Si-nmr measurements on oligomeric, polymeric, branched and cyclic siloxanes have appeared in the literature[181,182,183] as have the results of examinations of selected organosilicon compounds.[184]

3.2.2. ^{1}H- AND ^{13}C-NMR SPECTROSCOPIC STUDIES

3.2.2.a MODEL ORGANOSILOXANES

In the ^{1}H nmr spectra of the polymers described in this thesis, which have a $-CH_2CH_2R$ sidechain (R = SPh, SBu, PPh_2, Br, I), a large difference in chemical shifts for the methylene protons is observed. The silicon has a shielding effect on the adjacent methylene protons, creating a shift to higher field, and the R groups cause bonded methylene groups to resonate at lower field through deshielding effects.

In the ^{1}H-nmr spectra of compound (1), $Me_3SiO[MeSi(H)O]SiMe_3$ coupling effects were observed as described in section 3.2.1a.

The SiH proton resonance was reported[171] as an unresolved multiplet in 100MHz spectra, but in the high field spectrum of (1) (Table 3.4) a quartet centred at ca. 4.7ppm is seen. In addition, a pair of satellites with a $^{29}Si-^{1}H$ coupling of 236.3Hz appear as poorly resolved quartets. These satellites are only apparent on this one signal, so confirming three-bond coupling through the Me-Si-H moiety, where hydrogen has a net through-space deshielding effect compared to the methyl group itself. ^{13}C-nmr spectra revealed singlets for the $OSiMe_3$ and SiMe groups.

Studies at 400MHz on the vinylsiloxane (2a) revealed that the apparent singlet observed by Watts[171], could be resolved into 10 components as typically found for ABC spin systems (Section 3.2.1a). The ^{13}C-nmr spectrum of this compound showed single resonances for the SiMe and $OSiMe_3$ groups.

The ^{13}C-nmr spectrum of the phosphine functionalised trisiloxane (3) reveals coupling between the ^{31}P nucleus and the methylene and aromatic carbon atoms. The methylene resonances are doublets with coupling constants of 14.3 and 11.0Hz for the $-CH_2P$ and $\equiv SiCH_2-$ moieties respectively. Assignments of the aromatic signals and appropriate coupling constants are given in Table 3.4. The proton nmr spectrum of the $-CH_2CH_2SPh$ functionalised trisiloxane (4) shows an A_2X_2 splitting pattern of 14 identifiable components for the methylene groups. In view of the incomplete resolution of the multiplets, no attempt has been made to analyse these data further.

TABLE 3.4 ^{1}H AND ^{13}C-NMR SPECTRAL DATA FOR MODEL ORGANOSILOXANES[a]

Compound	OSiMe	SiMe	C1/H1[b]	C2/H2[b]	OTHERS	AROMATICS
(1)	0.15(18H) 1.60	0.15(3H) -0.42			4.63(1H,q, J(SiH) 236.3)	
(2a)	0.52(18H) 1.83	0.52(3H) -0.52	6.01(3H,m) 137.37	132.62		
(3)	0.13(18H) 1.75	0.13(3H) -0.63	0.58(2H,m) 12.99 (d, 11.0)	2.62(2H,m) 20.77 (d, 14.7)		7.27(10H,m) 138.6(d, 18.4 C3) 133.8(d, 19.1 C6) 132.6(d, 26.1 C4/4') 128.2(d, 4.1, C5/5')
(4)	0.08(18H) 1.75	0.08(3H) -0.20	0.78(2H,m) 17.90	2.92(2H,m) 28.32		7.33(5H,m) 137.0(C3) 129.1(C6), 128.8(C4/4') 125.7(C5/5')
(5)	0.08(18H)	0.08(3H)	0.82(2H,m)	2.49(2H,m)	2.53(2H,m,H3) 1.52(2H,m,H4) 1.39(2H,m,H5) 0.89(3H,t,H6)	
	1.67	-0.44	18.27	21.90	31.34(C3) 31.54(C4) 26.31(C5) 13.53(C6)	

[a] singlets unless stated otherwise

[b] numbered away from silicon atom

[c] substituents are numbered away from phosphorus atom (3) or sulphur atom (4) starting with 3.

3.2.2b POLYORGANOSILOXANES

^{13}C nmr data for all the functionalised linear polysiloxanes have been recorded and analysed, leading to the following generalisations (Table 3.5) concerning the chemical shifts of the methyl groups. These chemical shift ranges are somewhat narrower than those found for short-chain model siloxanes (Table 3.1).

TABLE 3.5 ^{13}C-NMR CHEMICAL SHIFTS FOR POLYSILOXANE METHYL GROUPS

Type	Chemical Shift (δppm rel. TMS)
Me_3SiO	1.82 ± 0.06
Me_2SiO	1.09 ± 0.01
$MeSi-(CH_2)_n-L$	-0.31- -0.58

In proton nmr spectra, the methyl groups appear as a broad, unresolved singlet in the region 0.01 - 0.25ppm. Full proton and ^{13}C-nmr spectral data for the functionalised polysiloxanes prepared during the course of these studies are listed in Table 3.6. Few are anomalous and warrant further detailed discussion. The ^{13}C-nmr data were in general most easily interpreted, and in the spectra of all siloxane polymers signals for each methylene group in the spacer chain, as well as other methylene groups in the molecules, were readily identified and assigned. Proton nmr data were less straightforward in some cases. Thus the splitting pattern of the ABC vinyl spin system in the ^{1}H-nmr spectrum of compound (7b) is virtually identical to that of its model analogue (2a), with at least 10 components identifiable in the region 5.8 - 6.2ppm. A similar splitting pattern

TABLE 3.6 ^{1}H AND ^{13}C-NMR DATA FOR SELECTED ORGANOPOLYSILOXANES

Compound	Me_3SiO	Me_2SiO	SiMe	C1/H1	C2/H2	C3/H3	Others[c]	Aromatics[d]
(6b)		0.01(15OH)		0.42(2H,t)	1.49(2H,q)	2.72(2H, t)	1.31(3H,s,NH,NH_2) 2.53(2H,t,H4) 2.58(2H, m, H5)	
	1.83	1.10	-0.57	15.11	23.77	42.00	52.60(C4) 53.09(C5)	
(7b)		0.10(16OH)		6.03(3H,m)				
	1.86	1.11	-0.57	137.24	132.75			
(8b)		0.15(16OH)		0.52(2H,m)	1.42(4H,m)		2.10(2H,m,H4) 5-6(3H,m,H5/H6)	
	1.86	1.10	-0.57	17.51	22.66	32.63	33.66(C4), 114.3(C6) 139.0(C5)	
(9b)		0.13(16OH)					0.40-2.20(11H,m) 5.70(2H,m,$CH=CH_2$)	
	1.83	1.08	-0.54	14.40	25.44		36.33(CH), 28.61, 29.75, 31.66 126.7(C=CH) 127.0(CH=C)	
(10b)		0.25(15OH)		0.75(2H,m)	1.88(2H,m)	2.80(2H,m)	7.27(5H,m)	
	1.89	1.10	-0.31	17.35	25.08	39.48		142.5(C3) 128.4(C6) 128.2(C4/4') 125.6(C5/5')
(11a)		0.04(15OH)		0.85(2H,t)	2.75(2H,t)	3.24(2H,s)	c	
	1.86	1.10	-0.56	17.81	24.04	33.42	c	

TABLE 3.6 (Contd.)

Compound	Me_3SiO	Me_3SiO	SiMe	C1/H1	C2/H2	C3/H3	Others[c]	Aromatics[d]
(12a)		0.11(150H)		0.67(2H,m)	1.71(2H,m)	2.56(2H,m)	1.32(1H,m,5H)	
	1.86	1.10	-0.52	16.61	27.87	28.00		
(13a)		0.13(150H)					4.74(1H,q, J(SiH)237.1)	
	1.84	1.09	-0.55					
(14a)		0.18(140H)		0.64(2H,m)	2.06(2H,m)			7.14(10H,m)
	1.85	1.10	-0.56	12.67(d,10.7)	20.82(d,14.6)			138.7(d,17.9,C3) 133.8(d,21.0,C6) 132.7(d,26.0,C4/4') 128.3(d,4.3,C5/5')
(15a)		0.30(150H)		1.11(2H,m)	3.15(2H,m)			7.24(5H,m)
	1.84	1.10	-0.50	18.00	28.51			137.4(C3) 129.1(C6)128.8 (C4/4') 125.7(C5/5')
(16)		0.12(160H)		0.92(2H,m)	2.55(2H,m)		2.62(2H,m,H3) 1.62(2H,m,H4) 1.47(2H,m,H5) 0.98(3H,t,H6)	
	1.79	1.08	-0.44	18.43	22.12	31.30	31.53(C4), 26.51(C5), 13.73(C6)	

TABLE 3.6 (Contd)

Compound	Me_3SiO	Me_3SiO	SiMe	C1/H1	C2/H2	C3/H3	Others[c]	Aromatics[d]
(17)[e]		0.10(160H)		0.60 - 2.30(12H,m,H1-6)				7.10(10H,m)
(18)		0.11(155H)		0.50 - 1.90(12H,m,H1-6)				7.20(5H,m)
	1.84	1.06	-0.50	17.73	23.04	28.73	29.33(C4), 32.22(C5), 33.88(C6)	138.1(C3), 129.4(C6) 129.0(C4/4') 125.9(C5/5')
(19)[e]		0.25(160H)		1.39(2H,m)	3.55(2H,m)			
(20)[e]		0.21(160H)		1.31(2H,m)	3.22(2H,m)			

[a] Singlets unless stated otherwise

[b] All integral values quoted ± 5H

[c] Numbered away from silicon atom

[d] Numbered away from phosphorus atom or sulphur atom starting with 3

[e] ^{13}C-nmr spectra poorly resolved.

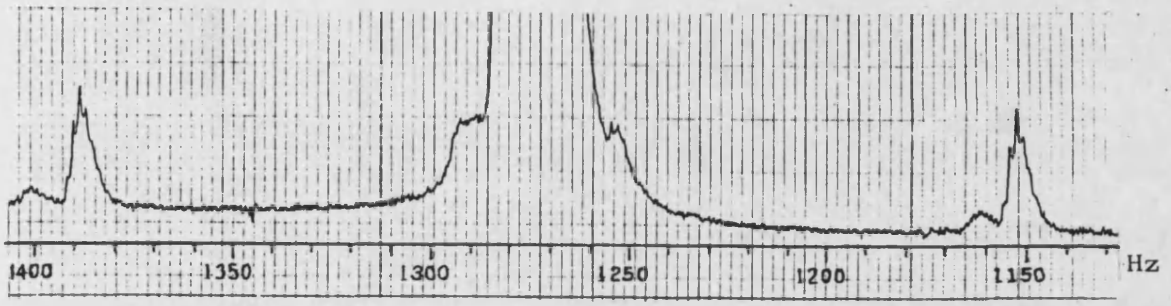
centred at ca. 5.5ppm is evident in the ^{1}H-nmr spectrum of the $-(CH_2)_4CH=CH_2$ functionalised polysiloxane (8b) and the methylene signals occur as overlapping multiplets in the region 0.5 - 2.1ppm. The ^{1}H-nmr spectral bands of the $-(CH_2)_2C_6H_9$ and $-(CH_2)_3C_6H_5$ functionalised polysiloxanes (9b) and (10b) respectively were rather broad, probably because of the presence of traces of residual platinum. Consequently detailed assignments were difficult to make. For the former, the olefinic signals appear as a broad singlet at around 5.7ppm, and the methylene protons appear as a complex multiplet centred at 1.30ppm.

As in the ^{1}H-nmr spectrum of the model compound $Me_3SiO(MeSi(H)O)SiMe_3$ (1), a quartet is observed at 4.75ppm in the spectrum of compound (13a) which is assigned to SiH protons. The coupling constant of 237.1Hz is also similar to that observed for (1). The $-(CH_2)_2PPh_2$ and $-(CH_2)_2SPh$ functionalised polysiloxanes (14a) and (15a) exhibit similar spectral features to their model analogues (3) and (4), although the proton nmr spectrum of (14a) was poorly resolved in comparison with the model compound.

3.2.3 ^{29}Si-NMR SPECTROSCOPIC STUDIES

The ^{29}Si-nmr spectrum of (1), $Me_3SiO[MeSi(H)O]SiMe_3$, is tabulated in Table 3.7. The $OSiMe_3$ signal occurs as a deciplet with a Si-H coupling constant of 53.1Hz. The Me-Si-H moiety resonates as a doublet of quartets with couplings of 236.8Hz and 22.6Hz. The former coupling confirms the assignment made for the proton nmr spectrum of (1) which exhibits a pair of weak satellites with a coupling constant of 236.3Hz. In the spectra of model organosiloxanes

^{1}H-nmr spectrum of (1)



(2), (3) and (4), some evidence of coupling patterns could be seen but these were not clearly resolved and hence no definite assignments have been attempted. The ^{29}Si-nmr spectrum of (3), however, shows clear ^{29}Si - ^{31}P coupling in the MeSi($CH_2CH_2PPh_2$)O signal, which occurs as a doublet centred at -22.6ppm with a coupling constant of 29.5Hz. Similar coupling effects were apparent in the spectrum of (4).

For the organopolysiloxanes, (6b) - (16) the Me_2SiO moiety has a chemical shift of between -21 and -23ppm and the Me_3SiO moiety resonates at δ6.7 to 7.7ppm. For (6b), (8b), (9b) and (10b), no separate signals were found for the functionalised silicon centre and it is likely that they are present under the intense Me_2SiO signal. MeSi(R)O signals for (7b), (11a), (12a), (13a), (14a), (15a) and (16) were observed in the region of -23.4 to -37.9ppm.

TABLE 3.7 ^{29}Si-NMR DATA FOR ORGANOSILOXANES

Compound	Me_2SiO	Me_3SiO	$MeSi(R)O$[a]
(1)	-	9.49(dec.53.1)	-36.28(dq 236.8,22.6)
(2a)	-	7.37	-34.57
(3)	-	7.67	-22.61(d, 29.5)
(4)	-	6.76	-25.17
(5)	-	6.90	-25.40
(6b)	-22.48	7.66	-
(7b)	-21.86	7.34	-35.83
(8b)	-22.48	7.38	-
(9b)	-21.86	7.34	-
(10b)	-22.80	7.18	-
(11a)	-22.47	6.77	-25.36
(12a)	-22.03	7.16	-25.40
(13a)	-21.48	7.72	-37.12(dq 238.9, 22.8)
(14a)	-21.86	7.32	-23.67(d,27.5)
(15a)	-22.03	7.15	-23.41
(16)	-22.03	7.16	-25.29

[a] dq = doublet of quartets

3.2.4 ^{31}P-NMR SPECTROSCOPY

^{31}P-nmr spectra have been recorded for the $-(CH_2)_2PPh_2$ functionalised trisiloxane (3) and its long-chain analogue (14a). As expected,[83] each spectrum consists of a singlet (at +9.26 and +9.15ppm for (3) and (14a) respectively relative to 85% H_3PO_4 and following the IUPAC convention that positive values are to high frequency). An additional weak signal at -34.1ppm in the spectrum of (14a) is tentatively assigned to an impurity - probably the corresponding phosphine oxide produced by air oxidation of the material during preparation of the sample for nmr measurements.

3.3 INFRARED SPECTROSCOPY

Infrared absorptions for organosilicon compounds are well documented.[186] The most predominant bands which are characteristic of siloxanes occur in the region 1100 - 1000cm^{-1} and are assigned to the asymmetric Si-O-Si stretching mode. In infinite siloxane chains, absorption maxima occur near 1085cm^{-1} and 1020cm^{-1}. A summary of typical infrared absorptions for methyl containing organosiloxanes is listed in Table 3.8. Corresponding data for model siloxanes and selected polyorganosiloxanes are summarised in Tables 3.9 and 3.10 respectively. As well as the characteristic siloxane absorptions, the polymers exhibit absorptions typical of their functionalities (Table 3.11), although in the long chain polymers of 2 - 10mol% functionality these bands may appear only weakly.

TABLE 3.8 INFRARED ABSORPTION ASSIGNMENT FOR METHYLSILOXANES

Infrared Absorption Frequency (cm^{-1})	Group	Assignment
1100 - 1000	Si-O-Si	Si-O-Si asymmetric stretch
841, 755	Me_3Si	Me rocking vibration
850, 800	Me_2Si	Me rocking vibration
3000 - 2850	MeSi	C-H stretch
1440 - 1390	MeSi	C-H asymmetric bending mode
1280 - 1240	MeSi	C-H symmetric bending mode
870 - 750	MeSi	Me rocking vibration
865 - 715	MeSi	Si-C stretch
845, 745	Me_3SiO	Si-C stretch

TABLE 3.9 INFRARED ABSORPTION FREQUENCIES FOR MODEL ORGANOSILOXANES

Compound	Infrared Absorption Frequency (cm^{-1})
(1)	2970s, 2905w, 2160s, 1402w, 1253vs, 1055vs, 916s, 890sh, 840vs, 762s, 690w.
(2a)	3050m, 3021w, 2968vs, 2904m, 1593m, 1404s, 1256vs, 1053vs, 1020sh, 959m, 870m, 843vs, 797s, 754s, 685m, 630m.
(3)	3068w, 3050w, 2952s, 2895m, 1583w, 1478m, 1430m, 1411m, 1259s, 1182w, 1152m, 1055vs, 1000sh, 843vs, 796s, 782s, 754s, 740s, 722m, 695s
(4)	3070w, 3060w, 2968s, 2925m, 2901m, 1580m, 1479m, 1437m, 1412w, 1259vs, 1164m, 1060vs, 1026sh, 1010sh, 843vs, 798s, 784s, 758s, 740s, 692s

TABLE 3.10 INFRARED ABSORPTION FREQUENCY FOR SELECTED POLYORGANOSILOXANES

Compound	Infrared Absorption Frequency (cm^{-1})
(6b)	3300vw, 2965s, 2906m, 1590br, 1440w, 1410m, 1260vs, 1055vs, 968sh, 800vs, 760sh, 697m, 663m.
(7b)	3055w, 2955s, 2915m, 1593m, 1440m, 1410s, 1260vs, 1058vs, 965sh, 825vs, 762s, 694s, 664s.
(8b)	3075w, 2975s, 2940s, 2864m, 1638m, 1440w, 1410m, 1260vs, 1190w, 1095vs, 1030vs, 910m, 842s, 800vs, 760sh, 691w.
(9b)	3025m, 2972s, 2911m, 2848m, 1647w, 1438m, 1404m, 1257vs, 1200w, 1166sh, 1137sh, 1080vs, 1010vs, 861sh, 798vs, 751m, 693s, 655sh.
(10b)	3085m, 3060m, 3042s, 2958vs, 2941vs, 2863s, 1597m, 1580w, 1493m, 1452s, 1402m, 1340w, 1258vs, 1173s,1159s,1080vs,1020vs, 962m, 920w, 902w, 842vs, 797vs, 763vs, 700vs, 650sh.
(12a)	3025w, 2971s, 2915m, 2802w, 2580vw, 1440w, 1410m, 1262vs, 1053vs, 965sh, 810vs, 762s, 694m, 658m.
(13a)	2970s, 2927s, 2856m, 2160w, 1452w, 1410w, 1403sh, 1273w, 1260vs, 1090vs, 1021vs, 913m, 870m, 800vs, 760m, 700m, 689m, 659w.

TABLE 3.11 DIAGNOSTIC INFRARED ABSORPTION FREQUENCIES FOR FUNCTIONAL GROUPS

Compound	Absorption Frequency (cm^{-1})	Assignment
(1)	2160	Si-H stretch
	916, 890	Si-H bending mode
(2)	1593	C=C stretch
(3)	3068, 3050	aromatic C-H stretch
	1583, 1478	aromatic C=C skeletal stretch
(4)	3070, 3060	aromatic C-H stretch
	1580, 1479	aromatic C=C skeletal stretch
(6b)	3300	N-H stretch
	1590	primary NH_2 deformation
(8b)	1638	C=C stretch
(9b)	1640	C=C stretch
(10b)	1598, 1490	aromatic C=C skeletal stretch
(11a)	1713	C=O stretch
(12a)	2580	S-H stretch

3.4. GEL PERMEATION CHROMATOGRAPHY (GPC)

GPC is a valuable technique for fractionating a wide variety of both natural and synthetic polymers, and it may be used preparatively or as an analytical technique. A major difference between GPC and most other methods of fractionation is that separation is primarily based on molecular size, rather than chemical constitution. Thus larger molecules are eluted from the column first and the smaller ones at the end of the separation. For species with molecular weights greater than 1000, the polarity of the molecules becomes relatively unimportant, and separation is by size alone. Further details of the instrumentation employed are given in Appendix 2. Mean average molecular weights (M_w) were determined for a selection of functionalised polysiloxanes and the results are tabulated (Table 3.11). In preparative procedures, GPC studies complemented viscosity measurements as a means for determining whether equilibration of polymer reactants was complete. Furthermore, GPC traces also gave clear indications of the purity of the final products. For example, the presence of cyclic dimethylsiloxanes in the products was readily detected and was indicative of incomplete 'stripping' of the polysiloxanes. Although small errors in the measurement of the retention of the peaks will cause a relatively large error in the estimation of the absolute molecular weight, relative molecular weights were found to be very reproducible for identical samples. All figures quoted in Table 3.12 are average values of multiple measurements and are in the range $M_w \pm 50$.

TABLE 3.12 MEAN AVERAGE MOLECULAR WEIGHT DATA FOR SELECTED ORGANOPOLYSILOXANES

Compound	M_w	Expected M_w [a]
(6b)	3800	3886
(7b)	3510	3738
(8b)	4120	3850
(9b)	4260	3902
(10b)	4350	3922
(12a)	3800	3834
(13a)	3610	3686
(19)	4150	3900

[a] Based on the combining mol ratios of the reactants.

CHAPTER FOUR

METAL COMPLEXED MODEL SILOXANES AND POLYSILOXANES

4.1. SUMMARY

A range of catalytically active transition metal entities have been coordinated to a selection of the model organosiloxanes and organopolysiloxanes, whose syntheses and characterisation have been described in chapters two and three respectively. Metallated organosiloxanes containing the $-(CH_2)_3NH(CH_2)_2NH_2$, $-(CH_2)_2PPh_2$ and $-(CH_2)_2SPh$ ligand endings have been most extensively investigated and characterised using ^1H and ^{13}C nuclear magnetic resonance, together with infrared and electronic absorption spectroscopies where appropriate, with a view to determining the primary metal coordination sphere.

4.2. SYNTHETIC PROCEDURES

The diamine, phosphine and thiol functionalised polysiloxanes, (6b), (14a) and (15a) respectively, have proved to be very effective ligands for salts of the transition-metals platinum, palladium, rhodium, cobalt, copper, nickel, molybdenum, chromium, tungsten and iron. Synthetic routes to metallated compounds have involved either substitution reactions where ligands such as CO (equation 77) or RCN (R = alkyl or aryl) (equations78 and 79) are displaced from the reactant, or halide bridged splitting reactions (equation 80).

$$M(CO)_6 + L \rightarrow M(CO)_4(L) + 2CO \qquad (77)$$
$$L = (P)\text{-ethylenediamine})$$

$$MCl_2 2RCN + L \rightarrow MCl_2(L) + 2RCN \qquad (78)$$
$$L = (P)\text{-ethylenediamine}$$

$$[M(MeCN)_x]^{2+}[(BF_4)_2]^{2-} + 3L \rightarrow [ML_3]^{2+}[BF_4]_2^{2-} + xMeCN \qquad (79)$$
$$L = (P)\text{-ethylenediamine}$$

$$[Rh(CO)_2Cl]_2 + 4L \rightarrow 2Rh(CO)Cl(L)_2 + 2CO \qquad (80)$$
$$L = (P)\text{-phosphine}$$

The initial complexes used together with the anchored metal moieties derived from them are listed in Table 4.1. Tables 4.2 - 4.5 list formulae for the metallated cyclic and model trisiloxanes, diamine functionalised-, phosphine functionalised-, and other functionalised polysiloxanes respectively.

TABLE 4.1 TRANSITION-METAL COMPLEXES USED IN METALLATION REACTIONS AND THEIR ANCHORED METAL MOIETIES

Metal Complex[a]	Anchored Metal Moiety
$Fe_2(CO)_9$	$Fe(CO)_4$
$FeCp(CO)_2X$[b] (187)	$FeCp(CO)_2$
$M(CO)_6$[c]	$M(CO)_4$
$MCl_2(MeCN)_2$[d] (188-190)	MCl_2
$[M(MeCN)_x][BF_4]_2$[e] (191-196)	$M(BF_4)_2$
$RhCl_3.xH_2O$	RhCl
$[Rh(CO)_2Cl]_2$ (197)	$Rh(CO)_2Cl$, Rh(CO)Cl
$[Ru_2(OAc)_4Cl]$ (198)	Ru(OAc)Cl
$M(OAc)_2.xH_2O$[f]	$M(OAc)_2$

[a] References for reactant preparation given in parentheses if the compound was not obtained commercially.

[b] X = Br, I.

[c] M = Mo, Cr, W.

[d] M = Pt, Pd, Co, Cu, Ni.

[e] M = Pt, x = 4; M = Pd, x = 4; M = Co, x = 6; M = Cu, x = 4; M = Ni, x = 6.5.

[f] M = Co, x = 4; M = Cu, x = 1; M = Ni, x = 4

TABLE 4.2 METALLATED CYCLIC AND MODEL SILOXANES

Compound	Formulation	Primary metal coordination sphere
(23)	$[MeSi(CH=CH_2)O]_4Fe(CO)_4$	$Fe(CO)_4(CH_2=CH\rightarrow$
(24)	$[MeSi(CH=CH_2)O]_4FeCp(CO)_2$	$FeCp(CO)_2(CH_2=CH\rightarrow$
(25)	$[(Me_3SiO)_2SiMe(CH_2CH_2PPh_2)]_2PtCl_2$	trans-$PtCl_2P_2$
(26)	$[(Me_3SiO)_2SiMe(CH_2CH_2PPh_2)]_2Rh(CO)Cl$	trans-$RhP_2(CO)Cl$
(27)	$[(Me_3SiO)_2SiMe(CH_2CH_2PPh_2)]_3RhCl$	$RhClP_3$
(28)	$[(Me_3SiO)_2SiMe(CH_2CH_2SPh)]_2Rh(CO)Cl$	trans-$RhS_2(CO)Cl$
(29)	$[(Me_3SiO)_2SiMe(CH_2CH_2SPh)]_3RhCl$	$RhClS_3$
(30)	$[(Me_3SiO)_2SiMe(CH_2CH_2PPh_2)]_3Ru(OAc)Cl$	$RuP_3Cl(O)$

TABLE 4.3 METALLATED POLYSILOXANES OF GENERAL FORMULA

$\{Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2CH_2NHCH_2CH_2NH_2)O]_2SiMe_3\}_xM$

Compound	x	Transition-metal Moiety (M)	N-atoms available/ M atom
(31)	1	$\{Mo(CO)_4\}_2$	2
(32)	1	$\{Cr(CO)_4\}_2$	2
(33)	1	$\{W(CO)_4\}_2$	2
(34)	1	$CoCl_2$	4
(35)	1	$CuCl_2$	4
(36)	1	$NiCl_2$	4
(37)	3	$\{Co(BF_4)_2\}_2$	6
(38)	3	$\{Cu(BF_4)_2\}_2$	6
(39)	3	$\{Ni(BF_4)_2\}_2$	6
(40)	1	$\{PtCl_2\}_2$	2
(41)	1	$\{PdCl_2\}_2$	2
(42)	1	$Pt(BF_4)_2$	4
(43)	1	$Pd(BF_4)_2$	4
(44)	1	$Co(OAc)_2$	4
(45)	1	$Cu(OAc)_2$	4
(46)	1	$Ni(OAc)_2$	4
(47)	3	$\{RhCl\}_4$	3
(48)	1	$Rh(CO)Cl$	2
(49)	1	$CuCl$	4

TABLE 4.4 METALLATED POLYSILOXANES OF GENERAL FORMULA

$\{Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2PPh_2)O]_2SiMe_3\}_xM$

Compound	x	Transition-metal Moiety	P atoms available/ M atom
(50)	1	$PtCl_2$	2
(51)	1	$PdCl_2$	2
(52)	2	$Pt(BF_4)_2$	4
(53)	2	$Pd(BF_4)_2$	4
(54)	1	Rh(CO)Cl	2
(55)	3	$\{RhCl\}_2$	3
(56)	3	{Ru(OAc)Cl}	3

TABLE 4.5 METALLATED POLYSILOXANES OF GENERAL FORMULA

$\{Me_3SiO[Me_2SiO]_{46}[MeSi(R)O]_2\}_xM$

Compound	R	x	M	S atoms available /M atom
(57)	$-CH_2CH_2SPh$	1	$Rh(CO)Cl$	2
(58)	$-CH_2CH_2SPh$	3	$\{RhCl\}_2$	3
(59)	$-(CH_2)_6SPh$	1	$Rh(CO)Cl$	2
(60)	$-(CH_2)_6SPh$	3	$\{RhCl\}_2$	3
(61)	$-CH_2CH_2SBu$	1	$Rh(CO)Cl$	2
(62)	$-CH_2CH_2SBu$	3	$\{RhCl\}_2$	3
(63)	$-(CH_2)_2SCH_2COOH$	1	$CoCl_2$	2
(64)	$-(CH_2)_2SCH_2COOH$	1	$CuCl_2$	2
(65)	$-(CH_2)_2SCH_2COOH$	1	$NiCl_2$	2

In view of the air and moisture sensitivity of some of the polymers, all of the preparations and purification procedures were conducted under an inert atmosphere using degassed, absolute solvents and high purity starting materials. Of the metallated products, the metal carbonyl derivatives proved to be very unstable and decomposed even on storage at room temperature under a nitrogen atmosphere.

Experimental procedures are described only for the metallation of 50D.P. 4mol% polymers, although metallations have been carried out on the majority of higher or lower mole percentage polymers whose syntheses are described in Chapter Two. As would be expected for metallated polymers with the same degree of polymerisation and the same metal to ligand ratio, the lower mole percentage functionalised fluids had lower viscosities than their counterparts with a higher concentration of functionalities.

Separation of unreacted organosiloxanes from metallated products has been achieved by column chromatography for the metallated model trisiloxanes (25), (26) and (27).

Most of the metallation reactions of organofunctionalised polysiloxanes were carried out with a <u>two-fold</u> excess of ligand present. However, the figures given in Tables 4.3 - 4.5 correlate to the metallated species <u>as if no excess ligand had been employed</u> in order to give a better indication of the metal coordination sphere.

The excess of ligand functionalised material and relatively forcing reaction conditions have been employed to achieve complete coordination of the transition-metal species. Further to this, an excess of functionalised polysiloxane has also served to produce mobile and solvent-soluble metallated polymers which would otherwise be gel-like and very insoluble in normal organic solvents.

Elemental analyses for several of the metallated siloxanes could not be obtained due to their instability.

4.2.1. METALLATION OF DIAMINE FUNCTIONALISED POLYSILOXANES

Investigations on the metallation of the $-(CH_2)_3NHCH_2CH_2NH_2$ functionalised polysiloxane (6b) were first carried out using $M(CO)_6$(M = Mo, Cr or W) in order to determine how easily and completely this polymer could be metallated. Reaction of a two-fold excess of (6b) (for the formation of (31)) in refluxing toluene with $Mo(CO)_6$ yielded a red-brown solution from which product (31) was isolated as a red-brown fluid on removal of solvent in vacuo. Infrared spectroscopy (Table 4.8) indicated that no unreacted $Mo(CO)_6$ remained and four absorptions characteristic of the cis-$L_2Mo(CO)_4$ moiety were present. Analogous species were isolated from the reaction of (6b) with $Cr(CO)_6$ and $W(CO)_6$ (equation 77) giving products (32) and (33) respectively. The metallated products (31), (32) and (33) were unstable and decomposed even under a nitrogen atmosphere, and consequently no further carbonyl derivatives of 6(a), (c) or (d) were prepared or used in subsequent studies.

The ligating ability of the diamine functionalised polysiloxane (6b) towards the transition-metals platinum, palladium, cobalt, copper and nickel have also been examined. Metals were introduced via substitution of MeCN in $MCl_2(MeCN)_2$ and $[M(MeCN)_x][BF_4]_2$, as indicated in equations (2) and (3), and by their direct reaction with (6b) in refluxing acetone or dichloromethane. The transition-metal entities $M(OAc)_2.xH_2O$ (M = Co, Cu and Ni) have also been coordinated to (6b) for comparison of their catalytic activity in oxidative coupling reactions with the metal(II) chloride species. No attempt has been made, however, to fully characterise these three materials.

4.2.2. METALLATION OF PHOSPHINE AND THIOL FUNCTIONALISED MODEL TRISILOXANES AND POLYSILOXANES

The phosphine functionalised model trisiloxane (3) and polysiloxane (14a) reacted similarly with transition-metal entities. Metallations using $MCl_2(MeCN)_2$ and $[M(MeCN)_4][BF_4]_2$ (M = Pt, Pd) were achieved by heating the reactants under reflux in acetone with reaction times of up to 16h. The long reaction times were a result of the poor solubility of the metal-methyl cyanide complexes in the organic solvents used.

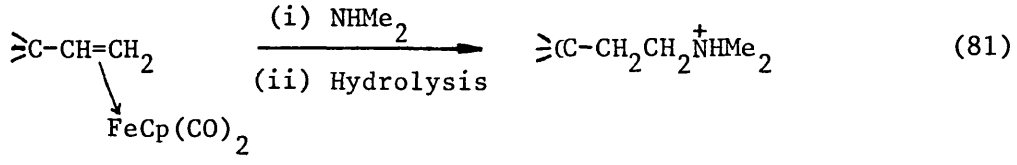
The rhodium-metallated trisiloxanes (26) and (28) have been prepared using variations of the methods described by Brzezinska and Cullen[83]. Heating $[Rh(CO)_2Cl]_2$ and (3) or (4) in refluxing benzene for 4h yielded yellow solids for (26) and (28) respectively on removal of solvent in vacuo. Infrared spectroscopy indicating the absence of starting material and the present of a Rh(CO)Cl

anchored moiety. In the preparations of (27) and (29), it was necessary to dissolve finely-divided $RhCl_3.xH_2O$ in a minimum amount of ethanol prior to addition to (3) or (4) dissolved in toluene, as the reaction was otherwise very slow (72h). Reflux of the reactants yielded yellow-brown solids on solvent removal in vacuo. The metallated trisiloxanes (26) and (27) were purified by column chromatography on fluorosil employing an acetone/petroleum ether mixture as eluent. Products (28) and (29) decomposed on attempts to purify them by this procedure. The rhodium-metallated polysiloxanes were prepared similarly to their trisiloxane analogues, however, purification by column chromatography was not possible as the metallated polymer was held on the column.

4.2.3. MISCELLANEOUS METALLATIONS

4.2.3a. INTERACTION OF THE VINYL FUNCTIONALISED CYCLIC SILOXANE WITH IRON CARBONYL DERIVATIVES

Initial investigations in the research programme centred on attempts to determine whether the vinylic group of $[MeSi(CH=CH_2)O]_4$ would coordinate effectively to transition metals, and if it could be activated by metallation and so transformed to a more useful ligating group. Previous work[199] has shown that iron carbonyl derivatives coordinate strongly to related vinyl ligands, and in some cases activate them towards nucleophilic attack. Consequently



(81)

$[MeSi(CH=CH_2)O]_4$ was reacted with both $Fe_2(CO)_9$ and $[FeCp(CO)_2X]$ (X = Br, I) in order to investigate these possibilities. The first

of these reactions produced a very air-sensitive yellow oil, shown by analysis and infrared spectroscopy (Table 4.6) to be product (23), in which one carbonyl group of $Fe(CO)_5$ has undergone substitution by one of the four vinyl groups. Examination of the reactivity of (23) proved extremely difficult due to the ease with which the product decomposed in the presence of traces of air or moisture. Consequently attempts were made to prepare an iron cyclopentadienyl derivative instead, using the following well-established procedure for making cationic olefinic complexes of the $FeCp(CO)_2$ entitity (equation 82).

$$CpFe(CO)_2X + [Me(CH=CH_2)SiO]_4 \xrightarrow[(ii)\ H_2O,\ PF_6]{(i)\ ZnCl_2} \{FeCp(CO)_2[Me(CH=CH_2)SiO]_4\}^+ PF_6^- \qquad (82)$$

(X = Br, I)

On reaction of $[CpFe(CO)_2X]$ (X = Br, I) with the vinyl functionalised cyclic material in the presence of $ZnBr_2$ or $AlCl_3$, (24) was formed. However hydrolysis of the $ZnBr_4^{2-}$ or AlX_4^- ion in the presence of PF_6^- resulted in complete decomposition of the product. In order to avoid the intermediacy of zinc or aluminium salts, an alternative procedure was attempted[200] as outlined below (equation 83).

$$FeCp(CO)_2I \xrightarrow{AgBF_4} [FeCp(CO)_2\ solvent]BF_4 + AgI \qquad (83)$$

$$\downarrow [Me(CH=CH_2)SiO]_4,\ Et_2O$$

$$[FeCp(CO)_2\{Me(CH=CH_2)SiO\}_4]^+BF_4^-$$

Although there was some spectroscopic evidence that the required product was formed, all attempts to isolate the complex were unsuccessful so these reactions were abandoned.

4.2.3b. REACTIONS OF THE DIAMINE-COPPER(II) SYSTEM (35)

A preliminary attempt was made to determine whether simple metal-redox reactions could be effected on $CuCl_2$ bound to the diamine functionalised polymer (6b). This system was chosen as the $d^9 \rightarrow d^{10}$ change expected for a Cu(II)→Cu(I) reduction process would result in a marked colour change. On bubbling sulphur dioxide through a solution of the metallated polymer in toluene the initial blue solution turned green and then colourless, indicative of the formation of a copper(I) species. When the solution was degassed by refluxing under nitrogen, a green colour reappeared showing the copper(I) species to be unstable and to disproportionate or be reoxidised perhaps by extraction of oxygen from the siloxane, as the reaction was carried out in the absence of O_2 gas. As no redox studies on such systems have been carried out, further qualitative and quantitative investigations of this behaviour are warranted.

4.2.3c. EXTRACTION OF METAL IONS FROM AQUEOUS SOLUTION BY THE DIAMINE FUNCTIONALISED POLYSILOXANE

Preliminary studies have shown that the diamine functionalised polysiloxane (6b) is capable of the effective extraction of ions from aqueous metal chloride and metal acetate solutions. Cobalt, copper and nickel salts were used and they were present in a large excess. In these reactions, it was clear from the polymer colour change that metal ions quickly coordinated to the polysiloxane, and throughout the extraction, the polymer remained immiscible with water. Following extraction (five minutes standing at room temperature) the two phases were separated and the metallated polymer substrate dissolved in toluene. The product was dried with molecular

sieves and the concentration of metal present in the polymer was determined quantitatively.[201] These analyses showed that a ligand to metal ratio of 6-8:1 was achieved in these simple extraction procedures irrespective of the metal salt used.

4.2.3d. METALLATION OF 3-THIA-4-CARBOXYBUTYL FUNCTIONALISED POLYSILOXANE

Very brief investigations on the ligating ability of the polymer (11a) showed that coordination of the transition-metal entities $MCl_2(MeCN)_2$ (M = Co, Cu and Ni) was likely to have occurred in a manner similar to that for the $-(CH_2)_3NH(CH_2)_2NH_2$ functionalised polysiloxanes, with the $-SCH_2COOH$ entity acting as a bidentate ligand. However, unlike their diamine analogues (34) and (37) the cobalt(II) species proved to be air stable. Due to time constraints, these complexes were not studied further and greater examination is warranted in a future study.

4.2.3e FAILED METALLATIONS

Reaction of the functionalised polysiloxanes (7b) (8b), (9a), (10b) and (13a) with $MCl_2(MeCN)_2$ (M = Pt, Co, Cu or Ni) for 48h in refluxing acetone, toluene, or dichloromethane resulted in no or negligible coordination of the metal to the polymers.

4.3 SPECTRAL CHARACTERISATION OF METALLATED CYCLIC AND MODEL SILOXANES, AND POLYSILOXANES

4.3.1. INFRARED SPECTROSCOPY

The infrared spectra of the metallated model organosiloxanes have been recorded in order to provide structural information on

metal carbonyl and metal halide containing species which may be compared and extrapolated to the polymer attached analogues. Absorptions due to the siloxane backbone of the substrate were essentially unaffected by complex formation.

4.3.1a MODEL AND CYCLIC ORGANOSILOXANES

The infrared spectra of (23), the iron tetracarbonyl π-complex of methylvinylcyclosiloxane, shows carbonyl absorptions at 2070, 2030, 1988 and 1971 cm^{-1} indicative of monosubstitution of one equatorial carbonyl group in the trigonal bipyramidal $Fe(CO)_5$ molecule. The weak ν(C=C) bond due to coordinated $CH=CH_2$ expected for this product was not observed, although a large ν(C=C) shift of 200-270cm^{-1} has been reported for $Fe(CO)_4$ derivatives of other vinylsiloxanes[8] and vinylsilanes.[202] A weak absorption at 1598cm^{-1}, corresponding to uncoordinated vinyl groups was, however, observed.

The infrared spectrum of compound (26) shows a single intense absorption at 1965cm^{-1} which is characteristic of similar trans-$Rh(CO)Cl(L)_2$ (L = tertiary phosphine) complexes in which the two phosphine ligands are equivalent[85,204]. A single carbonyl absorption at approximately 1980cm^{-1} would be anticipated for the cis-$Rh(CO)Cl(L)_2$ species[205]. A single broad carbonyl absorption at 1979cm^{-1} was observed for compound (28) which is not diagnostic specifically of either a cis- or trans-Rh(CO)Cl anchored moiety.

TABLE 4.6 INFRARED CARBONYL ABSORPTION DATA FOR METALLATED MODEL AND CYCLIC SILOXANES

Compound No.	Primary metal coordination sphere	Representation for CO stretches	(C≡O) (cm^{-1})
(23)	$Fe(CO)_4(CH_2{=}CH\rightarrow$	$2A_1 + B_1 + B_2$	2070, 2031 1988, 1971
(26)	trans-$RhP_2(CO)Cl$	A_1	1965
(28)	trans-$RhS_2(CO)Cl$	A_1	1979

TABLE 4.7 INFRARED (M-Cl) STRETCHING FREQUENCIES FOR HALO-COMPOUNDS

Compound No.	Primary metal coordination sphere	stretch	ν(M-Cl)(cm^{-1})
(25)	trans-$PtCl_2P_2$	(Pt-Cl)	341
(27)	$RhClP_3$	(Rh-Cl)	257
-[a]	trans-$PtCl_2P_2$	(Pt-Cl)	326-340
-[a]	cis-$PtCl_2P_2$	(Pt-Cl)	302-312 and 277-293

[a] Reference data[203]

The ν(Rh-Cl) modes expected for compounds (26) and (28) were not observed in the far-infrared region of their spectra, presumably due to masking by other absorptions, but in compound (27) the (Rh-Cl) stretch was observed as a very weak absorption at 257cm^{-1}, in agreement with literature data on related L_3RhCl species[83]. The (Pt-Cl) stretch occurred at 341cm^{-1} in the infrared spectrum of compound (25), which is similar to data recorded by Bruner and Bailar on trans-$PtCl_2$(P-ligand)$_2$.[203]

4.3.1b ORGANOPOLYSILOXANES

Infrared spectra recorded for metallated polysiloxanes were only of diagnostic value for metal-carbonyl containing moieties, as metal-chlorine stretches (which were weak in the spectra of the metallated model compounds) were not visible at all in the spectra of polyorganosiloxanes containing metal halides. The carbonyl absorptions for compounds (31), (32) and (33) are tabulated in Table 4.8. The spectra all contained four carbonyl absorptions in similar positions to those found for cis-$M(CO)_4$en (M = Mo, Cr, W) species[206].

TABLE 4.8 INFRARED CARBONYL ABSORPTION DATA FOR COMPOUNDS (31), (32) AND (33)

ν(C≡O) (cm^{-1})				
(31)[a]	(32)[a]	(33)[a]	$Mo(CO)_4en$[b]	Representation of CO stretch
2008	2006	2004	2015	A_1
1862	1860	1858	1864	A_1
1890	1885	1882	1890	B_1
1818	1814	1814	1818	B_2

[a] measured as a nujol mull [b] reference data, measured in $CHCl_3$

The carbonyl absorptions of the phosphine and thiol functionalised polymers following treatment with $[Rh(CO)_2Cl]_2$ are listed in Table 4.9. All are consistent with a trans-$Rh(CO)Cl(L)_2$ moiety, as expected from the result of studies on the trisiloxane derivatives described earlier.

TABLE 4.9 INFRARED CARBONYL ABSORPTION DATA FOR Rh(CO)Cl ANCHORED MOIETIES

Compound	$\nu(C\equiv O)$ (cm^{-1})	Representation of (CO) stretch
(54)	1962	A_1
(57)	1981	A_1
(59)	1984	A_1
(61)	1979	A_1

4.3.2 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Both ^1H and ^{13}C-nmr spectra have been recorded for the metallated cyclic and model siloxanes (23)-(29) for comparison with data for the free siloxanes. The shift differences were, as expected, greatest for those ligand endings involved most closely in bonding to the metal complex, and these differences diminish with increasing distance from the metal centre. All of the metallated cyclic and model siloxanes had reasonably good solubilities in deuterated solvents, and high sample concentrations and overnight accumulations of ^{13}C-nmr data were often needed in order to observe methylene and carbonyl resonances. Metallated linear polysiloxanes

contained a considerably lower concentration of metal than the model compounds, and also exhibited decreased solubility in deuterated solvents, as well as having an excess of uncoordinated ligand present (in order to produce fluid materials). Consequently their ^{1}H and ^{13}C-nmr spectra were either broadened due to overlapping resonances, decomposition, exchange processes or showed uncoordinated as well as coordinated ligand.

Spectral results for the metallated model organosiloxanes (25)-(29) are listed in Table 4.6. The ^{1}H- and ^{13}C-nmr data for siloxyphosphines (25), (26) and (27) have been reported previously[83,171]. In the ^{13}C-nmr spectrum of (26), coupling of the ^{31}P nucleus with both the aromatic carbons and the methylene group adjacent to the phosphorus centre is evident with complex splitting patterns being observed. The single carbonyl resonates as a doublet centred at δ188.1 with ^{1}J (^{103}Rh-^{13}C) coupling of 71.1Hz, which is consistent with a planar trans-configuration for the $Rh(CO)Cl(L)_2$ unit of this complex, in agreement with conclusions based on infrared spectral data. Well defined doublets are also observed for the methylene groups in the ^{13}C-nmr spectrum of the rhodium complex (27) with phosphorus-carbon coupling constants of 8.1 and 67.2Hz for C_1 and C_2 respectively (numbering away from the silicon atom). With the exception of spectra from complex (29) in which J(Rh-C) coupling was clearly observed, the other complexes produced poorly resolved spectra, or decomposed during the accumulation of ^{13}C spectral data.

TABLE 4.10 ^{1}H- AND ^{13}C-NMR SPECTRAL DATA FOR SELECTED METALLATED MODEL ORGANOSILOXANES

Compound	OSiMe	SiMe	C^1/H^1	C^2/H^2	Others	Aromatics
(25)	0.03(36H,s)	-0.01(6H,s)	0.60(m) (total 8H)	2.38(m)		7.41(m) 7.58(m) (total 20H)
	1.75	-0.68	12.28	25.44		132.8(t,4.9) 130.4, 128.1(t,4.9)
(26)	0.08(36H,s)	0.04(6H,s)	0.93(m) (total 8H)	2.86(m)		7.16(m), 7.90(m) (total 20H)
	2.30	0.26	12.71	22.81	188.1(d,71.1)	135.6, 134.8, 134.3, 134.2, 133.9, 130.0, 129.9,128.7,128.4
(27)	0.16(54H,s)	0.12(9H,s)	1.10(m) (total 12H)	2.90(m)		7.14(m), 7.95(m) (total 30H)
	1.60	-0.90	7.83(d 8.1)	20.21(d 67.2)		134.9(d,2.3,C1) 132.1(d,9.1,C2/2') 127.4(d,9.3,C3/3') 130.0(d,8.4,C4)
(28)	0.04(36H,s)	0.00(6H,s)	0.89(m) (total 8H)	2.97(m)		7.24, 7.76 (total 10H)
	1.00	-0.23	17.52	36.20	182.8(d,74.5)	132.5(C3) 129.4(C6) 129.1(C4/4') 128.8(C5/5')
(29)	0.04(54H,s)	0.04(9H,s)	0.86(m) (total 12H)	3.24(m)		7.24(m), 7.76(m) (total 15H)
	1.04	-0.99	18.35	29.71		133.4(C3) 129.8(C6) 129.3(C4/4') 125.5(C5/5')

4.3.3. ELECTRONIC ABSORPTION SPECTROSCOPY

The majority of transition-metal complexes are coloured due to absorption bands in the visible region of their electronic spectrum. Almost invariably, this is accompanied by absorption in the adjacent near-ultraviolet and sometimes in the near-infrared regions. The successful development of theories for interpreting spectra which are associated with compounds of metals having an incompletely filled d-subshell has led to the measurement of the visible spectrum to be considered an essential part of the characterisation of any new complex. The visible spectra for the cobalt, copper and nickel metallated DIAMINE functionalised polysiloxanes (34) - (39) were measured over the range 190 - 2500nm.

4.2.3a COBALT-DIAMINE SYSTEMS

The $-(CH_2)_3NH(CH_2)_2NH_2$ functionalised polysiloxanes metallated with Co(II) species were shown to be very air unstable. Thus the initially pink CH_2Cl_2 solution of (34) with μ_{max} at 470nm rapidly turned brown with the development of a new band at 500nm. After 24h. storage or air exposure, the solution was red-brown with only the latter band apparent in its spectrum. This is consistent with literature data on analogous CoN_4Cl_2 complexes undergoing oxidation to cis-octahedral Co(III) species (Table 4.11). Alternatively, it is possible that a μ-peroxo species is formed asit is well established that many cobalt(II) complexes containing N-ligands will take up molecular oxygen very readily in aqueous solutions under basic reaction conditions to give bi-nuclear complexes containing the $\mu\text{-}O_2^{2-}$ ion. [207-209]

TABLE 4.11 REFLECTANCE SPECTRA FOR COBALT COMPLEXES[a]

Transition	(34)	(37)	[b] $[Co(en)_3]^{2+}$	[b] $[Co_2(en)_5O_2]^{4+}$	[b] $cis[Co(en)_2Cl_2]C$
$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	470[c]	470[c]	460		
$^1T_{1g} \leftarrow {}^1A_{1g}$	500[d]	500[d]		470	525

a Band maxima in nm

b Reference data

c Initial data

d After exposure to oxygen or on standing

Such products are brown, diamagnetic ions of general formula $[N_5CoO_2CoN_5]^{4+}$ (N = N-ligand), which can be further transformed into dibridged μ-amido-μ-peroxo dicobalt(III) species or oxidised to paramagnetic μ-superoxo $[N_5CoO_2N_5]^{5+}$ ions.[210] There is insufficient evidence from absorption spectroscopy to decide whether or not the Co(II)→Co(III) transformation occurs with retention of an O_2 species.

4.3.3b COPPER-DIAMINE SYSTEMS

Because of the relatively low symmetry (i.e. less than cubic) of the ligand environments in which the Cu^{2+} ion is characteristically found, detailed interpretation of the spectral and magnetic properties of these species is difficult. Most copper(II) complexes are blue or green showing absorptions between 600 and 900nm, and the copper metallated diamine functionalised polymers (35) and (38) are green and show a single broad absorption band centred at around 600nm. If the complex were perfectly octahedral, only a single band due to the transition $^2T_{2g} \leftarrow {}^2E_g$ would be expected. However, the

observed band is very broad and asymmetric and probably involves several overlapping absorptions. A distorted octahedral coordination is probable in view of the excess ligand present.[207,211, 212]

4.2.3c NICKEL-DIAMINE SYSTEMS

The nickel metallated polymers (36) and (39) are violet and show three bands in their visible spectrum, (Table 4.12).

TABLE 4.12 REFLECTANCE SPECTRA OF OCTAHEDRAL NICKEL(II)[a]

Transition	(36)	(39)	[b] $[Ni(en)_3]^{2+}$	[b] $[Ni(py)_4Cl_2]$
$^3T_{2g} \leftarrow {}^3A_{2g}$	950	900	900	925
$^3T_{1g}(F) \leftarrow {}^3A_{2g}$	570	565	550	628
$^3T_{1g}(P) \leftarrow {}^3A_{2g}$	340	340	335	-

[a] Band maxima in nm

[b] Reference data[207,213,214]

The position of the bands and the colour of the complexes are consistent with that expected for octahedrally coordinated nickel(II) complexes. Either $[Ni(en)_3]^{2+}$ or $[Ni((en)_2Cl_2]$ species may be present for (36), but for the purpose of labelling, the latter has been assumed.

4.3.4. ELECTRON SPIN RESONANCE SPECTROSCOPY

It was hoped that esr measurements could be used in conjunction with electronic spectroscopy for the interpretation of paramagnetic transition-metal ion coordination preferences in the polymers. Complexes (34) and (37) contain d^7 metal ions but showed only one very broad absorption either at room temperature or in a low temperature methylcyclohexane glass. Very broad single resonances were also observed for the d^9 Cu(II) species present in (35) and (38). No signals were observed for any of the Ni(II) or Co(III) containing derivatives. Attempts to determine whether Co(III) was present as a $\mu\text{-}O_2^{2-}$ complex in (34) and (37) by oxidation with a variety of strong oxidants to produce an esr active $\mu\text{-}O_2^{-}$ species were also unsuccessful.

4.4. EXPERIMENTAL

4.4.1. METALLATED MODEL COMPOUNDS

$[(Me_3SiO)_2SiMe(CH_2CH_2PPh_2)]_2PtCl_2$ (25)

Compound (3) (0.22g, 0.52mmol) dissolved in acetone ($4cm^3$) was added to $PtCl_2(MeCN)_2$ (0.090g, 0.26mmol) in acetone ($8cm^3$) and heated under reflux (56^oC) for 16h. The solvent was removed in vacuo and the mixture separated by column chromatography on fluorosil, eluting first with hexane and then ethyl acetate. White crystals were obtained on recrystallisation from acetone/hexane. (0.101g, 35%) (Found: C, 47.2; H, 6.80. $C_{42}H_{70}Cl_2O_4P_2PtSi_6$ requires C, 44.4; H, 6.17%).

$[(Me_3SiO)_2SiMe(CH_2CH_2PPh_2)]_2RhCOCl$ (26)

To a degassed solution of $[Rh(CO)_2Cl]_2$ (0.024g, 0.062mmol) in benzene ($15cm^3$) was added a solution of (3) (0.10g, 0.25mmol) in benzene ($5cm^3$). The mixture was heated under reflux for 4h until infrared spectroscopy indicated complete reaction of the starting material had occurred. The solvent was removed *in vacuo* yielding a yellow solid. TLC using an acetone/petroleum ether (b.p. 40 - 60°C) mixture (1:9^v/v) as the eluent indicated the presence of only one component (0.085g, 68%) (Found: C, 51.1; H, 6.95. $C_{43}H_{70}ClO_5P_2RhSi_6$ requires C, 49.8; H, 6.76%).

$[(Me_3SiO)_2SiMe(CH_2CH_2PPh_2)]_3RhCl.$ (27)

To $RhCl_3.xH_2O$ (0.016g, 0.060mmol) dissolved in a minimum amount of ethanol ($0.5cm^3$) was added (3) (0.075g, 0.18mmol) in toluene ($25cm^3$). The reactants were heated to reflux (110°C) for 4h. The solvent was removed *in vacuo* and the mixture separated by column chromatography on fluorosil using acetone/petroleum ether (b.p. 40 - 60°C), the product eluting as a yellow-brown band (0.042g, 50%) (Found: C, 51.8; H, 7.20. $C_{63}H_{105}ClO_6P_3RhSi_9$ requires C, 52.5; H, 7.29%).

$[(Me_3SiO)_2SiMe(CH_2CH_2SPh)]_2Rh(CO)Cl$ (28)

To a solution of (4) (0.57g, 1.60mmol) in benzene ($10cm^3$) was added $[Rh(CO)_2Cl]_2$ (0.16g, 0.40mmol) in benzene ($5cm^3$). The mixture was heated under reflux for 4h. until ν(CO) of the starting material had disappeared. The solution was filtered, the solvent removed *in vacuo* and the mixture separated by column chromatography on fluorosil using hexane and then ethyl acetate. The yellow band was collected from which the product was isolated as an orange-brown

solid (0.49g, 69%) (Found: C, 43.3; H, 6.90. $C_{31}H_{60}ClO_5RhS_2Si_6$ requires C, 42.2; H, 6.80%).

$[(Me_3SiO)_2Si(CH_2CH_2SPh)]_3RhCl$ (29)

To $RhCl_3.xH_2O$ (0.32g, 1.20mmol) dissolved in a minimum amount of ethanol ($0.5cm^3$) was added a solution of (4) (1.29g, 3.60mmol) in benzene ($20cm^3$). The mixture was heated under reflux for 6h. and then filtered. The solvents were evaporated under vacuum and the mixture separated by column chromatography on fluorosil, eluting with acetone/petroleum ether (b.p. 40 - 60°C) mixture 1:9(^{v}/v)). The product was isolated as a brown solid (1.10g, 75%). (Found: C, 45.8; H, 7.68. $C_{45}H_{90}ClO_6RhS_3Si_9$ requires C, 45.2; H, 7.53%).

4.4.2. METALLATED POLYSILOXANES

A two-fold excess of ligand has been used in all metallation reactions. The formulae given at the head of each preparation in this section represent the true formulae of the metallated polymer. However, the empirical formulae calculated for analysis requirements reflect the presence of the appropriate excess of the polymer. Some metallated polymers of very limited stability did not analyse reproducibly for C, H and/or N .

$\{Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2CH_2NHCH_2CH_2NH_2)O]_2SiMe_3\}[Mo(CO)_4]_2$ (31)

To a two-fold excess of the 50D.P. 4mol% diamine functionalised polysiloxane (6b) (3.89g, 1.0mmol) dissolved in toluene ($15cm^3$) was added $Mo(CO)_6$ (0.26g, 1.0mmol). The reactants were heated under reflux (110°C) for 4h. and yielded a viscous red-brown fluid on removal of solvent in vacuo. Infrared spectroscopy indicated no unreacted

hexacarbonyl to be present. The compound decomposed under a nitrogen atmosphere in 48h. infrared spectroscopy indicating the loss of carbonyl absorptions. (Found: C, 32.8; H, 7.89; N, 1.46. $C_{228}H_{652}Mo_2N_8O_{106}Si_{100}$ requires C, 33.4; H, 7.96; N, 1.37%).

$\{Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2CH_2NHCH_2CH_2NH_2)O]_2SiMe_3\}[Cr(CO)_4]_2$ (32)

In a similar procedure to that used for (31), $Cr(CO)_6$ (0.22g, 1.0mmol) was reacted with a two-fold excess of (6b) (3.89g, 1.0mmol) yielding a purple viscous fluid. Infrared spectroscopy showed no unreacted carbonyl to be present. The product was extremely unstable and decomposed in 24h. under an inert atmosphere with loss of carbon monoxide. No analytical data was obtained. Infrared data is given in Table 4.8.

$\{Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2CH_2NHCH_2CH_2NH_2)O]_2SiMe_3\}[W(CO)_4]_2$ (33)

A mixture of $W(CO)_6$ (0.35g, 1.0mmol) and (6b) (3.89g, 1.0mmol) was heated to reflux in toluene ($15cm^3$) for 4h. The product was obtained as an air-unstable orange-red oil which contained no unreacted hexacarbonyl as shown by infrared spectroscopy. The product decomposed in 12h. in a nitrogen atmosphere with loss of carbon monoxide. Table 4.8 contains ν(CO) data.

$\{Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2CH_2NHCH_2CH_2NH_2)O]_2SiMe_3\}CoCl_2$ (34)

To a two-fold excess of (6b) (2.33g, 0.60mmol) in CH_2Cl_2 ($15cm^3$) was added $CoCl_2(MeCN)_2$ (0.064g, 0.30mmol) dissolved in CH_2Cl_2 ($5cm^3$). The solution was heated under reflux under rigorously aneorobic conditions (40^oC) for 4h. so yielding a pink solution. On removal of solvent in vacuo a pink viscous oil was obtained (2.4g) which rapidly turned brown on exposure to air. On prolonged exposure to air (48h.) the fluid became red-brown. In view of the instability of the product,

no analysis was attempted.

$\{Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2CH_2NHCH_2CH_2NH_2)O]_2SiMe_3\}CuCl_2$ (35)

In an identical procedure to that for (34) above, $CuCl_2(MeCN)_2$ (0.065g, 0.30mmol) was added to a two-fold excess of (6b) (2.33g, 0.60mmol) employing CH_2Cl_2 as solvent. Following removal of solvent *in vacuo* an air stable viscous green fluid was obtained (2.3g) (Found: C, 33.5; H, 8.23; N, 1.31. $C_{220}H_{652}Cl_2CuN_8O_{98}Si_{100}$ requires C, 33.4; H, 8.25; N, 1.42%).

$\{Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2CH_2NHCH_2CH_2NH_2)O]_2SiMe_3\}NiCl_2$ (36)

The polymer (6b) (2.33g,0.60mmol) in CH_2Cl_2 ($15cm^3$) was mixed with $NiCl_2(MeCN)_2$ (0.064g, 0.30mmol) and heated at reflux temperatures for 4 hours. Removal of solvent *in vacuo* yielded an air stable violet viscous fluid (2.3g) (Found: C, 33.5; H, 8.26; N, 1.26. $C_{220}H_{652}Cl_2N_8NiO_{98}Si_{100}$ requires C, 33.4; H, 8.25; N, 1.42%).

$\{Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2CH_2NHCH_2CH_2NH_2)O]_2SiMe_3\}_3[Co(BF_4)_2]_2$ (37)

To a two-fold excess of (6b) (2.33g, 0.60mmol) in CH_2Cl_2 ($15cm^3$) was added $[Co(MeCN)_6][BF_4]_2$ (0.096g, 0.20mmol) in CH_2Cl_2 ($5cm^3$). The solution was heated to reflux temperatures (40^oC) and held at this temperature for 4h. yielding a viscous orange fluid on removal of solvent *in vacuo*. On exposure to air the fluid rapidly became orange-brown. On prolonged storage (48h.) the fluid became red-orange.

$\{Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2CH_2NHCH_2CH_2NH_2)O]_2SiMe_3\}_3[Cu(BF_4)_2]_2$ (38)

In an identical procedure to that used above, (6b) (2.33g, 0.60mmol) was reacted with $[Cu(MeCN)_4][BF_4]_2$ (0.08g, 0.20mmol). Removal of solvent in vacuo yielded a viscous green fluid.

$\{Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2CH_2NHCH_2CH_2NH_2)O]_2SiMe_3\}_3[Ni(BF_4)_2]_2$ (39)

Reaction of (6b) (2.33g, 0.60mmol) for 4h. in refluxing CH_2Cl_2 ($20cm^3$) with $[Ni(MeCN)_6][BF_4]_2$. 0.5MeCN (0.10g, 0.20mmol) yielded a viscous violet fluid on removal of solvent in vacuo. (Found: C, 33.5; H, 8.20; N, 1.20. $C_{660}H_{1956}B_4F_{16}N_{24}Ni_2O_{294}Si_{300}$ requires C, 33.3; H, 8.22; N, 1.41%).

$\{Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2CH_2NHCH_2CH_2NH_2)O]_2SiMe_3\}[PtCl_2]_2$ (40)

To a two-fold excess of (6b) (1.01g, 0.26mmol) in acetone ($15cm^3$) was added $PtCl_2(MeCN)_2$ (0.090g, 0.26mmol). The reactants were heated under reflux for 24h. Following filtration, the solvent was removed in vacuo yielding a viscous yellow fluid. (1.0g). (Found: C, 31.6; H, 8.00; N, 1.31. $C_{220}H_{652}Cl_4N_8Pt_2O_{98}Si_{100}$ requires C, 31.8; H, 7.85; N, 1.35%).

$\{Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2CH_2NHCH_2CH_2NH_2)O]_2SiMe_3\}[PdCl_2]_2$ (41)

In an identical procedure to that used for (40), a viscous yellow fluid (2.3g) was obtained on heating under reflux a mixture of (6b) (2.33g, 0.60mmol) and $PdCl_2(MeCN)_2$ (0.15g, 0.60mmol).

$\{Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2CH_2NHCH_2CH_2NH_2)O]_2SiMe_3\}Pt(BF_4)_2$ (42)

This material was prepared in an analogous manner to that given for fluid (40), by heating under reflux (6b) (2.33g, 0.60mmol) and $Pt(MeCN)_4(BF_4)_2$ (0.16g, 0.30mmol) in acetone ($20cm^3$). After filtration and removal of solvent in vacuo, a yellow fluid (2.2g) remained.

$\{Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2CH_2NHCH_2CH_2NH_2)O]_2SiMe_3\}Pd(BF_4)_2$ (43)

Compound (6b) (2.33g, 0.60mmol) and $[Pd(MeCN)_4][BF_4]_2$ (0.13g, 0.30mmol) were reacted as above to yield a viscous yellow fluid (2.3g).

$\{Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2CH_2NHCH_2CH_2NH_2)O]_2SiMe_3\}Co(OAc)_2$ (44)

To $Co(OAc)_2.4H_2O$ (0.12g, 0.5mmol) suspended in EtOH ($15cm^3$) was added (6b) (3.89g, 1.0mmol) dissolved in dichloromethane ($20cm^3$). The mixture was heated under reflux for 4h. and then filtered and solvent removal in vacuo to yield a mobile brown fluid. No evidence of an intermediate pink colouration (cf. $CoCl_2$ product) was obtained.

$\{Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2CH_2NHCH_2CH_2NH_2)O]_2SiMe_3\}Cu(OAc)_2$ (45)

A similar procedure to that given above was used to prepare (44). Starting from $Cu(OAc)_2.H_2O$ (0.10g, 0.5mmol) a viscous blue fluid was formed as the final product.

$\underline{\{Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2CH_2NHCH_2CH_2NH_2)O]_2SiMe_3\}Ni(OAc)_2}$ (46)

Reaction as above with $Ni(OAc)_2.4H_2O$ (0.12g, 0.5mmol) in place of the copper salt yielded a viscous blue-violet fluid.

None of the metal acetate complexes were analysed. Their stoichiometries are based solely on the reactant molar ratios.

$\underline{\{Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2CH_2NHCH_2CH_2NH_2)O]_2SiMe_3\}_3[RhCl]_4}$ (47)

A mixture of $RhCl_3.xH_2O$ (0.021g, 0.080mmol) dissolved in ethanol ($0.5cm^3$), (6b) (0.47g, 0.12mmol) and benzene ($20cm^3$) was heated under reflux for 4h. The solution was filtered and the solvent removed <u>in vacuo</u> so yielding a homogeneous brown fluid (0.48g). The metallated polymer decomposed on 24h. storage in an inert atmosphere.

$\underline{\{Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2CH_2NHCH_2CH_2NH_2)O]_2SiMe_3\}[Rh(CO)Cl]_2}$ (48)

A solution of $[Rh(CO)_2Cl]_2$ (0.12g, 0.30mmol) and a two-fold excess of (6b) (2.33g, 0.60mmol) in benzene ($15cm^3$) were heated under reflux for 4h. until $\nu(C\equiv O)$ of the starting material disappeared. The solvent was removed <u>in vacuo</u> so yielding a viscous brown oil (2.4g). The metallated polymer decomposed in 24h. under an inert atmosphere.

$\underline{\{Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2PPh_2)O]_2SiMe_3\}PtCl_2}$ (50)

This metallated polymer was prepared in an analogous manner to that described for (25). An excess of compound (14a) (1.23g, 0.30mmol) in acetone ($10cm^3$) was added to $PtCl_2(MeCN)_2$ (0.052g, 0.15mmol) and the mixture heated under reflux for 12h. Following filtration, removal of solvent <u>in vacuo</u> yielded a viscous clear yellow fluid

(1.20g) (Found: C, 36.1; H, 7.74. $C_{256}H_{656}Cl_2O_{98}PtSi_{100}$ requires C, 36.8; H, 7.85%).

$\{Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2PPh_2)O]_2SiMe_3\}PdCl_2$ (51)

To $PdCl_2(MeCN)_2$ (0.039g, 0.15mmol) in anhydrous acetone ($15cm^3$) was added (14a) (1.23g, 0.30mmol) in acetone ($10cm^3$). After heating under reflux for 12h. and subsequent filtration, the solvent was removed under vacuum so yielding a clear and viscous yellow fluid (1.20g).

$\{Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2PPh_2)O]_2SiMe_3\}_2Pt(BF_4)_2$ (52)

The title metal-complexed polysiloxanes was prepared using a two-fold excess of polymer (14a) (2.47g, 0.60mmol) dissolved in acetone ($15cm^3$) and $[Pt(MeCN)_4][BF_4]_2$ (0.080g, 0.15mmol). The mixture was heated under reflux for 12h. The solution was filtered and the solvent evaporated in vacuo to give the product as a viscous and clear yellow fluid (2.40g). (Found: C, 34.6; H, 7.71. $C_{512}H_{1312}B_2F_8O_{196}P_8PtSi_{200}$ requires C, 36.5; H, 7.81%).

$\{Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2PPh_2)O]_2SiMe_3\}_2Pd(BF_4)_2$ (53)

By employing a similar procedure to that used for (46), the above compound was prepared from $[Pd(MeCN)_4][BF_4]_2$ (0.067g, 0.15mmol), (14a) (2.47g, 0.60mmol) with acetone ($25cm^3$) as solvent. The product was isolated as a clear, viscous yellow fluid (2.30g).

$\{Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2PPh_2)O]_2SiMe_3\}Rh(CO)Cl$ (54)

To a solution of $[Rh(CO)_2Cl]_2$ (0.058g, 0.15mmol) in benzene ($5cm^3$) was added a solution of (14a) (2.46g, 0.60mmol) in benzene ($10cm^3$). The mixture was heated under 4h. reflux until $\nu(C\equiv O)$ of the starting material disappeared. The solvent was removed in vacuo so yielding a viscous yellow oil (2.40g). (Found: C, 37.2; H, 7.94. $C_{257}H_{656}ClO_{99}P_4RhSi_{100}$ requires C, 36.8; H, 7.82%).

$\{Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2PPh_2)O]_2SiMe_3\}_3[RhCl]_2$ (55)

In an analogous manner to the preparation of (27), a mixture of $RhCl_3.xH_2O$ (0.052g, 0.20mmol) dissolved in ethanol ($0.5cm^3$), (14a) (2.47g, 0.60mmol) and benzene ($20cm^3$) was heated under reflux for 4h. The solution was filtered and the solvent removed in vacuo so yielding an orange-brown fluid (2.40g). (Found: C, 37.5; H, 7.88. $C_{768}H_{1968}Cl_2O_{294}P_{12}Rh_2Si_{300}$ requires C, 37.0; H, 7.89%).

$\{Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2SPh)O]_2SiMe_3\}Rh(CO)Cl$ (57)

In an analogous procedure to that described for (28), a solution of (15a) (2.37g, 0.60mmol) in benzene ($20cm^3$) was added $[Rh(CO)_2Cl]_2$ (0.058g, 0.15mmol) in benzene ($5cm^3$). After heating under reflux for 4h. $\nu(CO)$ of the starting material had disappeared. The solution was filtered and the solvent removed in vacuo so yielding an orange-brown fluid (2.40g). (Found: C, 35.1; H, 7.98. $C_{233}H_{636}ClO_{99}RhS_4Si_{100}$ requires C , 34.6; H, 7.87%). Compounds (59) and (61) were prepared similarly.

{$Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2SPh)O]_2SiMe_3$}$_3[RhCl]_2$ (58)

A mixture of $RhCl_3xH_2O$ (0.053g, 0.20mmol) dissolved in ethanol (0.5cm^3), and (15a) (2.37g, 0.60mmol) in benzene (25cm^3) were heated under reflux for 4h. The solvents were removed *in vacuo* after filtration. The product was obtained as a clear brown mobile fluid (2.30g). (Found: C, 35.6; H, 7.99. $C_{696}H_{1908}Cl_2O_{294}Rh_2S_{12}Si_{300}$ requires C, 34.8; H, 7.94%). Compounds (60) and (62) were prepared similarly. Complexes (63), (64) and (65) were prepared in an identical manner to that for their diamine analogues (34), (35) and (36). The metallated polymers were obtained as violet, green and green mobile fluids for the Co, Ni and Cu complexes respectively.

4.4.3 MISCELLANEOUS AND FAILED REACTIONS

{$[MeSi(CH=CH_2)O]_4$}$Fe(CO)_4$ (23)

A mixture of tetravinyltetramethylcyclosiloxane $[MeSi(CH=CH_2)O]_4$ (1.72g, 5.0mmol) and $Fe_2(CO)_9$ (0.91g, 2.5mmol) dissolved in dry hexane (15cm^3) were stirred at reflux temperatures (68^{o}C). After 4h. the yellow-green solution was filtered and the solvent removed *in vacuo*, so yielding an air sensitive yellow oil. TLC (hexane/silica) indicated the oil to be a single component. (Found: C, 38.3; H, 4.86. $C_{16}FeH_{24}O_8Si_4$ requires C, 37.5; H, 4.72%).

{$[MeSi(CH=CH_2)O]_4$}$FeCp(CO)_2$ (24)

To $[FeCp(CO)_2Br]$ (0.25g, 1.0mmol), finely ground $ZnCl_2$(0.41g, 3.0mmol) in CH_2Cl_2 (10cm^3), was added $[MeSi(CH=CH_2)O]_4$ (0.34g, 1.0mmol). The mixture was stirred at ambient temperature for 48h. On treatment with aqueous NH_4PF_6, the product decomposed (loss of ν(CO) signal).

$\underline{\{[MeSi(CH=CH_2)O]_4\}FeCp(CO)_2}$ (24)

The above was repeated employing $AlCl_3$ (0.39g, 3.0mmol) instead of $ZnCl_2$. Hydrolysis with aqueous NH_4PF_6 again resulted in decomposition.

$\underline{\{[MeSi(CH=CH_2)O]_4\}FeCp(CO)_2}$ (24)

A mixture of $[FeCp(CO)_2I]$ (1.50g, 4.9mmol) $AgBF_4$ (1.05g, 5.4mmol) and CH_2Cl_2 ($50cm^3$) was stirred at ambient temperature for 30 mins., generating the reactive intermediate $[FeCp(CO)_2]^+$ in solution. The mixture was filtered and $[MeSi(CH=CH_2)O]_4$ (5.0g, 14.7mmol) added. The solution was stirred for 1h. at room temperature until infrared spectroscopy indicated reaction to be complete. The solvent was removed <u>in vacuo</u> yielding a red oil. Attempts to purify the product by column chromatography on fluorosil using dichloromethane as eluent resulted in decomposition of the oil.

CHAPTER FIVE

METAL CONTAINING POLYSILOXANE DERIVATIVES AS CATALYSTS

5.1. SUMMARY

This chapter contains an account of some of the catalytic reactions of several of the polysiloxane supported transition-metal entities described previously. Studies were confined to olefin hydrosilylations, oxidative coupling of 2,6-disubstituted phenol and a very brief investigation of methanol dehydrogenation. It has been found that several polysiloxane supported catalysts are active for these reactions, with platinum and rhodium metallated phosphine functionalised polysiloxanes the most active for hydrosilylation reactions. In the hydrosilylation and dehydrogenation reactions, where comparisons between the catalytic activities of metallated model siloxanes and metallated polysiloxanes were made, no significant differences were observed.

5.2. CATALYTIC STUDIES

5.2.1. HYDROSILYLATION REACTIONS

Examination of the catalytic potential of supported catalysts in typical hydrosilylation reactions has been limited to platinum, rhodium, palladium and cobalt entities supported on diamine, phosphine and thiol functionalised siloxanes. These are all analogues of well-known homogeneous systems.[1] All of the supported catalysts were shown to be very soluble in the olefin-siloxane reaction mixtures, the catalyst system becoming homogeneous on addition. However, in order to obtain accurate weights of small amounts of catalyst, the neat metallated polymers have been diluted with toluene to provide a 0.10% $^{w}/_{w}$ solution of the metal species.

All of the polysiloxane supported catalysts have been prepared in the presence of a two-fold excess of ligand as described in Chapter Two, and consequently the metallated model siloxanes have also been introduced into reaction mixtures in the presence of an equimolar excess of ligand so that direct comparisons between the two systems could be made. All hydrosilylation reactions have been effected under a nitrogen atmosphere in order to prevent hydrolysis of SiH containing materials by atmospheric moisture. In order to check that hydrosilylations were not proceeding in the absence of added catalysts, blank reactions were carried out routinely.

Initially, the hydrosilylation reaction between $Me_3SiO[Me_2SiO]_3[MeSi(H)O]_5SiMe_3$ and a vinyl endblocked polydimethyl-siloxane (V.E.P.), $(CH=CH_2)Me_2SiO[Me_2SiO]_{50}SiMe_2(CH=CH_2)$ (available from Dow Corning Limited) was examined qualitatively to screen the various catalysts. The method involved heating the stirred reactants in the presence of each potential catalyst until 'gelling' (formation of a solid rubber) occurred. This procedure was used to determine the temperatures at which the catalysts became active, and based on this initial screening, the more active catalysts were investigated in hydrosilylation reactions involving $Me_3SiO[MeSi(H)O]SiMe_3$ (1) and 1-octene or 1-decene. These latter reactions were conveniently monitored using infrared spectroscopy in the Si-H stretching region ($2160cm^{-1}$) and by gas chromatography. These catalysts were, in general shown to be very effective at concentrations as low as 10^{-5} mole of metal species per mole of SiH reactant, consequently a catalyst concentration of 5×10^{-5} mole of metal species per mole of SiH compound was maintained in all reactions.

5.2.1a QUALITATIVE HYDROSILYLATION REACTIONS OF VINYL ENDBLOCKED POLYDIMETHYLSILOXANE (V.E.P.) WITH $Me_3SiO[Me_2SiO]_3[MeSi(H)O]_5SiMe_3$

Listed in Table 5.1 are the approximate temperatures at which gellation was deemed to have occurred on heating a 1:1 mol ratio of V.E.P. and $Me_3SiO[Me_2SiO]_3[MeSi(H)O]_5SiMe_3$ with a selection of siloxane supported catalysts.

TABLE 5.1 GELLATION TEMPERATURES IN THE HYDROSILYLATION REACTION OF V.E.P. AND $Me_3SiO[Me_2SiO]_3[MeSi(H)O]_5SiMe_3$

Compound	Polymer type[a]	Primary metal coordination sphere	Gellation Temperature (^oC)
(25)	P; M	$PtCl_2P_2$	100
(26)	P; M	$RhP_2(CO)Cl$	105-110
(27)	P; M	$RhClP_3$	120
(28)	T; M	$RhS_2(CO)Cl$	105-110
(29)	T; M	$RhClP_3$	115
(34)	D; P^1	$CoCl_2N_4$	>200
(37)	D; P^1	CoN_6	>200
(40)	D; P^1	$PtCl_2N_2$	>200
(42)	D; P^1	PtN_4	>200
(47)	D; P^1	$RhClN_3$	200
(48)	D; P^1	$Rh(CO)ClN_3$	170
(50)	P; P^1	$PtCl_2P_2$	100
(51)	P; P^1	$PdCl_2P_2$	180
(52)	P; P^1	PtP_4	105
(53)	P; P^1	PdP_4	180
(54)	P; P^1	$Rh(CO)ClP_2$	105-110
(55)	P; P^1	$RhClP_3$	120
(57)	T; P^1	$Rh(CO)ClS_2$	110

Table 5.1 Contd.

(58)	T; P^1	$RhClS_3$	120
(59)	T; P^1	$Rh(CO)ClS_2$	115
(61)	T; P^1	$Rh(CO)ClS_2$	110
QZ-7039[b]	-	-	110-120
Pt No.2[b]	-	-	25

[a] D = diamine, P = phosphine, T = thiol; M = model siloxane, P^1 = polysiloxane. [b] Dow Corning proprietary catalysts.

Despite the crude nature of this experiment, it proved very reliable for the qualitative determination of catalyst activities. Results showed the metallated $-(CH_2)_2PPh_2$ and $-(CH_2)_2SPh$ functionalised organosiloxanes (25) - (29),(50) - (55), (57) - (59) and (61) to be most active, causing gellation of the reactants in the temperature range 100 - 120°C. The diamine functionalised polysiloxane (6b) containing bound cobalt (compounds (34) and (37)), platinum (compounds (40) and (42)) and rhodium (compounds (47) and (48)) species were much less effective, gellation only occurring at temperatures greater than 170°C.

5.2.1b. HYDROSILYLATION REACTION OF 1-ALKENES AND $(Me_3SiO)_2Si(Me)H$ (1)

From the results listed in Table 5.1, it was clear that the more active catalysts were effective at temperatures around 110°C, so this temperature was chosen initially to examine the hydrosilylation reaction of (1) with 1-octene and 1-decene (equation 84). At 110°C and with concentrations of catalysts of 5×10^{-5} mole per mole of SiH,

both alkenes were hydrosilylated very efficiently in the presence of the platinum and rhodium metallated organosiloxanes (25), (28), (50), (54), (57) and (61).

$$(Me_3SiO)_2Si(Me)H + CH_3(CH_2)_xCH=CH_2 \xrightarrow{\text{catalyst}} (Me_3SiO)_2SiMe(CH_2)_{x+2}CH_3 \qquad (84)$$

(where x = 5 or 7, compounds (69) and (70) respectively).

The products of these reactions (69) and (70) have been isolated from the reaction mixtures(in which catalysts (25) and (50) were employed) by column chromatography, followed by distillation under reduced pressure. Table 5.2 lists analytical data and ^{1}H- and ^{13}C-nmr spectral data for both products. There was no evidence from ^{1}H and ^{13}C-nmr spectroscopy for CH and CH_3 moieties resulting from the Markownikoff addition of Si-H to the olefins.

The $PtCl_2$ metallated $-(CH_2)_2PPh_2$ functionalised model siloxane and polysiloxane derivatives (25) and (50) respectively, have proved to be the most effective catalysts, the reactions being 85% complete after 15 minutes (at $110^{o}C$) with no visual decomposition of the catalyst. The metallated model complex (25) was found to be no more active under these conditions than its polymeric analogue (50). Watts[171] noted differences in activity between similar materials which were attributed to the low solubility of the polymeric species in the reaction mixtures, which resulted in it being deposited onto the walls of the reaction vessel above the stirred liquid level and hence being removed from the site of the reaction. In the

TABLE 5.2 ANALYTICAL, ^{1}H and ^{13}C-NMR SPECTRAL DATA FOR HYDROSILYLATION PRODUCTS, $(Me_3SiO)_2Si(Me)(CH_2)_nCH_3$ (n = 7,9)

Compound	B.p. °C (mmHg)	Analysis (%)		^{1}H and ^{13}C NMR data (δppm rel. TMS)			
				Me_3SiO	MeSi	CH_2[b]	CH_3[b]
		C	H				
(69)	91 (1.2)	53.2(53.9)	11.2(11.4)	0.20(18H,s)	0.10(3H,s)	0.5-2.0(14H,m)	1.02(3H,m)
				1.90	-0.20	33.4(C7),33.3(C6) 32.2(C5),29.5(C4) 23.3(C3),22.9(C2) 17.9(C1)	14.2(C8)
(70)	114(1.2)	56.5(56.3)	11.6(11.6)	0.19(18H,s)	0.08(3H,s)	0.5-2.0(16H,m)	1.02(3H,m)
				1.85	-0.25	33.3(C9),32.8(C8) 32.1(C7),32.0(C6) 29.7(C5),29.6(C4) 23.3(C3),22.8(C2) 17.8(C1)	14.1(C10)

[a] Calculated data in parentheses

[b] Numbered away from silicon atom

hydrosilylation reactions carried out as described above, no such problems arose. Table 5.3 and figure 5.1 show basic kinetic data for a selection of the catalysts in the reaction of 1-decene and $(Me_3SiO)_2Si(Me)H$ at 110°C. Catalyst (50) was chosen for a more detailed study and its activity profile over the temperature range 45 - 110°C is shown in Table 5.4 and figure 5.2. The numerical data was obtained in the usual way by measuring the areas of the peaks in the GC traces of each reaction.

TABLE 5.3 DATA FOR REACTION TIME VERSUS PERCENTATE LOSS OF (1) USING SELECTED CATALYSTS AT 110°C

Reaction time (mins)	Percentage loss of (1) using various catalysts						
	(25)	(28)	(50)	(54)	(57)	(58)	(61)
5	37	11	37	26	11	12	14
10	58	27	60	48	27	29	34
15	84	48	85	64	48	42	52
30	>90	70	>90	85	70	60	77
60	>95	75	>95	79	75	60	80

TABLE 5.4 DATA FOR REACTION TIME VERSUS PERCENTAGE LOSS OF (1) USING CATALYST (50) AT VARIOUS TEMPERATURES

Reaction Time (mins)	Percentage loss of (1) at various temperatures[a] employing catalyst (50)					
	45	50	70	80	100	110
5	< 5	< 5	7	13	25	37
10	< 5	6	15	27	47	58
15	< 5	10	24	47	59	84
30	< 10	32	56	77	> 90	> 90
60	20	78	>90	>90	>95	>95
120	40	>90	>90	>95	>95	>95

[a] temperatures in °C

FIGURE 5.1 GRAPH OF SiH LOSS VERSUS TIME FOR THE HYDROSILYLATION REACTION BETWEEN $(Me_3SiO)_2Si(Me)H$ AND 1-DECENE AT 110^oC

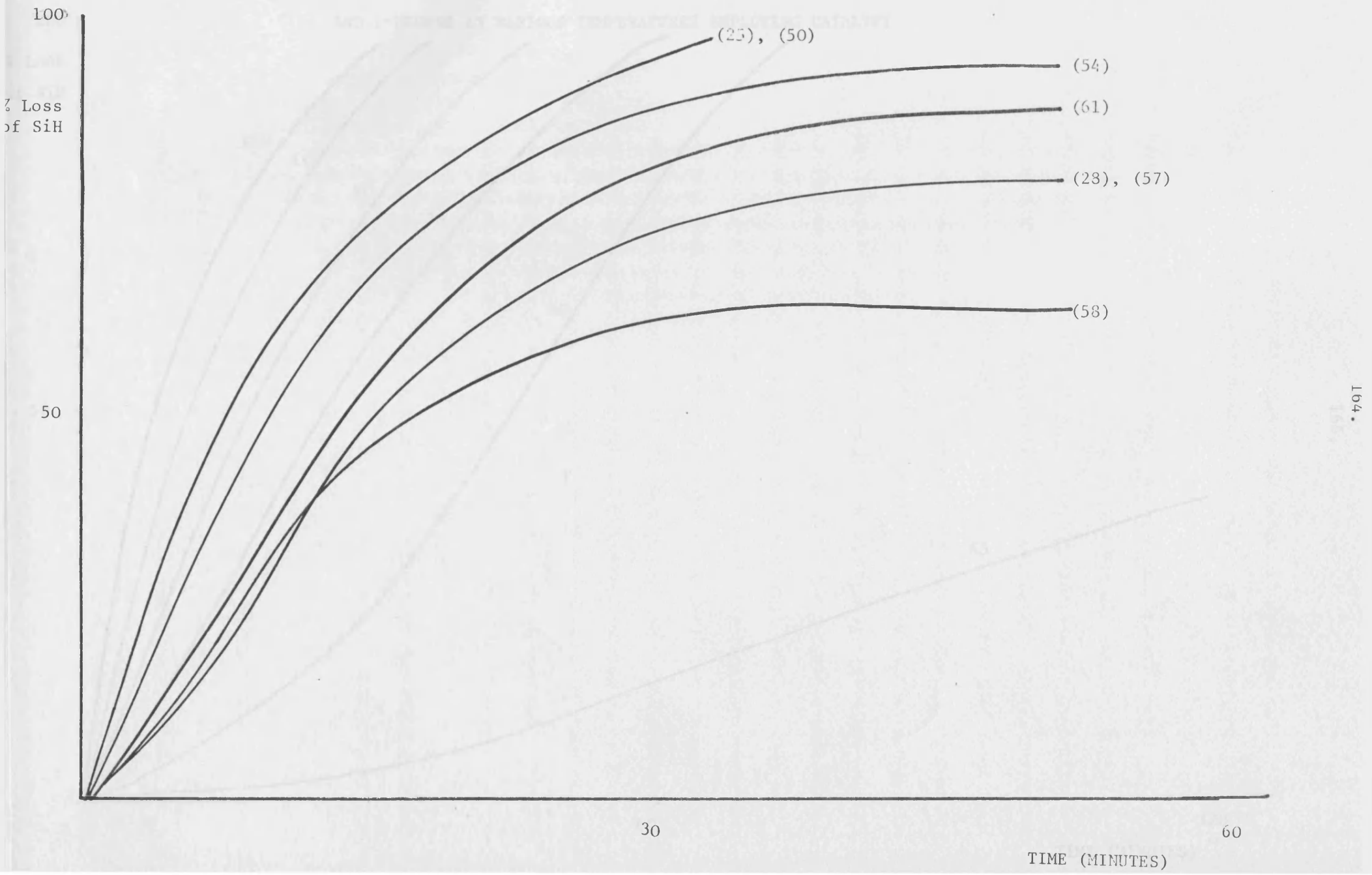
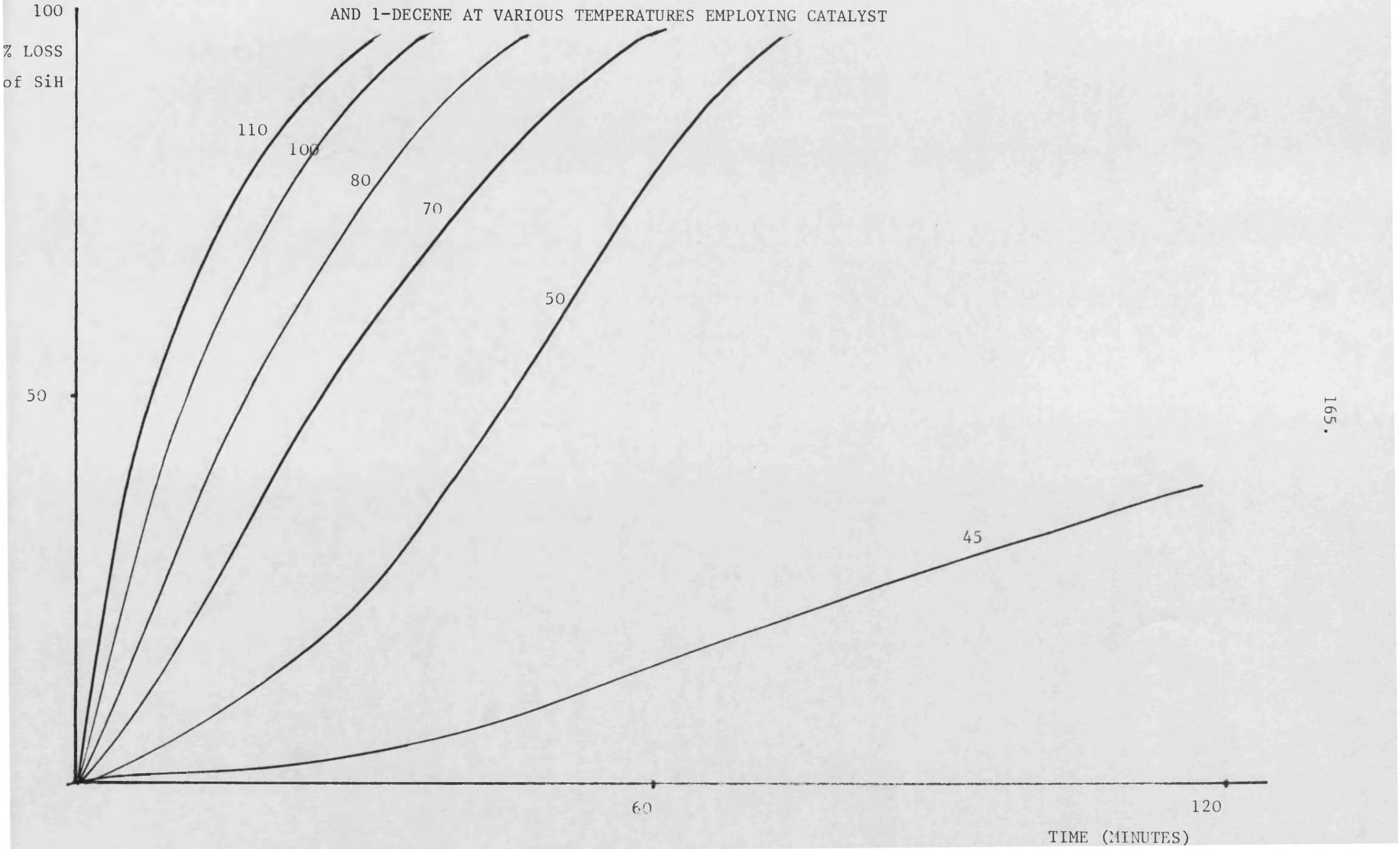


FIGURE 5.2 GRAPH OF SiH LOSS VERSUS TIME FOR THE HYDROSILYLATION REACTION BETWEEN $(Me_3SiO)_2Si(Me)H$ AND 1-DECENE AT VARIOUS TEMPERATURES EMPLOYING CATALYST



Plotting these data yield the curves illustrated in Figures 5.1 and 5.2 which show that only a short induction period occurs at higher reaction temperatures, this interval being more prolonged when lower reaction temperatures were employed. The occurrence of induction periods has been noted previously by Marciniec et al [126] in the hydrosilylation reaction of 1-hexene and triethoxysilane using Wilkinson's complex supported on phosphinated polyalkylsilsequioxanes. However, they noted that these induction periods were essentially temperature independent. The authors postulated that an essential feature of the reaction is the intermediacy of an octahedral catalytically active species consisting of two phosphines coordinated to a monomeric rhodium(III) centre. Data plotted in Figure 5.2 shows that catalyst (50) is very active at temperatures as low as 50°C, the reaction being more or less complete after 60 mins. Using the data from the curves for reactions carried out at 70, 80, 100 and 110°C, the Arrhenius activation energy for the process has been calculated to be 20.4kJ mol^{-1}. This figure for the polysiloxane supported Pt complex (50) contrasts with data by Marcineic et al [127] who determined activation energies for the Rh catalysed hydrosilylation of 1-hexene by triethoxysilane. They noted ΔE values of 71.2-73.3kJ mol^{-1} for reactions catalysed by rhodium supported siloxy-phosphine derivatives, which are higher by ca. 14kJ mol^{-1} than analogous reactions catalysed by homogeneous rhodium-phosphine complexes.

The rhodium catalysts (28), (29), (54), (57) and (58) decomposed slowly during the hydrosilylation reactions, with the deposition of a finely divided black solid on the wall of the reaction vessel as a result of leaching of a rhodium species from

the polymer. Brzezinska et al[84] have observed leaching in similar rhodium species and suggested that trace amounts of oxygen may aid the leaching mechanism, although all hydrosilylation reactions were carried out under an atmosphere of dry dinitrogen gas. The amount of leaching of the rhodium species from the metallated polysiloxanes was considerably less than from their model analogues, in agreement with observations by other authors[85,171].

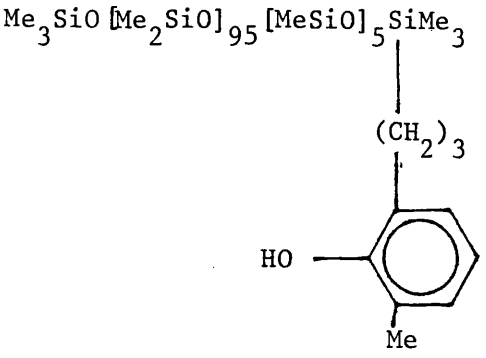
Noticeable during hydrosilylations catalysed by rhodium(I) chloride anchored moieties, was the formation of a new unreactive vinyl species which was detected in the proton nmr spectrum (δ = 6.1ppm) of the reaction mixture. It is feasible that a competing isomerisation reaction is occurring. Attempts to isolate this material which was formed only in very small quantities was unsuccessful using either column chromatography or distillation procedures. The isomerisation of but-1-ene to cis- and trans-but-2-ene has been reported[215] in the presence of supported liquid-phase and solid catalysts containing $RhCl_3$. It is well-known that terminal alkenes will undergo hydrosilylation much more readily than internal alkenes. In those cases where internal alkenes react, isomerisation to a terminal alkene may precede hydrosilylation. A steric influence is demonstrated by the observation that trans-2-pentene will not easily participate in hydrosilylations[216]. Indeed, we found no reaction after 3h. at 110°C between a mixture of trans-5-decene and $(Me_3SiO)_2Si(Me)H$ employing (58) as the catalyst, further supporting the possible formation of an internal alkene to explain the nmr observations.

The metallated siloxanes (25) and (50) containing the $PtCl_2$ anchored moiety appear the most active catalysts so far prepared. Surprisingly, Watts[171] observed no catalytic activity for (25), although reaction conditions were different in that a completely metallated complex was used as catalyst, whereas in this study a two-fold excess of ligand groups was present in the polymer. It seems possible that a fast metal-ligand exchange process is encouraged by the excess free ligand, and that the catalytic activity is associated with the transient "free" metal complex. Unfortunately there was insufficient time to investigate this possibility. Examples of platinum species containing diphenylphosphine oxide ligands of general formula $[Pt(H)(Ph_2PO)(Ph_2POH)(PPh_3)]$ have recently been successfully isolated and identified as catalysts in hydroformylation reactions[154] The diphenylphosphine ligand of the siloxanes (3) and (14a) is very air sensitive. It is also possible that some of the excess ligand present in the metallated polymer may have oxidised yielding similar species, although this explanation seems unlikely to account in total for the unexpectedly high activities of (25) and (50).

5.2.2. OXIDATIVE COUPLING REACTIONS

An oxidative coupling reaction catalysed by a basic copper salt-pyridine complex has been patented[217] in which organosilicon polymers containing phenolic residues are cured (Scheme 15, Chapter 1, Section 1.3.6). The compositions produced are useful as encapsulating agents and calking compositions and are of commercial interest to Dow Corning Limited. It was thought that

Cu-, Co- and Ni(II) when bound to the $-(CH_2)_3NH(CH_2)_2NH_2$ functionalised polymer (6b) may prove to be catalytically active for the curing of compound (XXXIV) which was obtained from Dow Corning Limited.



(XXXIV)

The metallated polymers investigated as catalysts have included (34), (35), (36), (44), (45) and (46) in the presence of a two-fold excess of ligand. The oxidative coupling reactions were carried out by simply heating compound (XXXIV) and the catalyst in air. No or negligible curing has been achieved at room temperature, but the rate was found to be accelerated by the application of heat. The reactions have also been attempted in the presence of catalyst, but in a sealed tube under a dinitrogen atmosphere. No reaction occurred in 5 days at 70°C under these conditions so confirming the necessity of oxygen for the reactions to proceed. Listed in Table 5.3 are the metallated polymers and solvents that have been employed in the course of the metallation process. This solvent was removed in vacuo before addition of the metallated polymers to the hydroxyphenyl substrate. Table 5.3 also lists the gellation times at 70°C. Although active, these catalysts were poor in comparison with Dow Corning catalysts, which can cause curing at

room temperature within seconds. Subsequently, no further investigations of this particular system were carried out.

TABLE 5.3 CURING TIMES FOR OXIDATIVE COUPLING REACTIONS

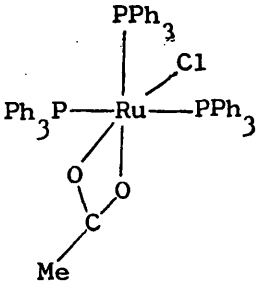
Catalyst	Solvent	Gellation time at 70°C (Hours)
(34)	CH_2Cl_2	2
(34)	H_2O	2
(34)	EtOH	2
(35)	CH_2Cl_2	6
(35)	H_2O	6
(35)	EtOH	6
(36)	CH_2Cl_2	6
(36)	H_2O	6
(36)	EtOH	6
(44)	EtOH	6
(45)	EtOH	6
(46)	EtOH	6

5.2.3 DEHYDROGENATION OF METHANOL

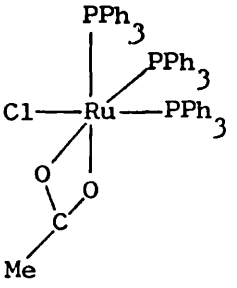
Preliminary qualitative investigations have been carried out on the homogeneous dehydrogenation of methanol (Equation 85) catalysed by ruthenium-phosphine complexes as described by Shinoda et al[142] (Chapter 1, Section 1.3.4), and also using the $-(CH_2)_2PPh_2$ functionalised model siloxane and polysiloxane materials (3) and (14a) respectively. On heating a solution of $[Ru_2(OAc)_4Cl]$ and triphenylphosphine dissolved in anhydrous methanol, the colour of the reaction mixture changed from

$$MeOH \rightarrow HCHO + H_2 \qquad (85)$$

brown to orange-yellow. From this orange-yellow solution Shinoda et al[142] isolated a mononuclear diamagnetic ruthenium complex, $[Ru(OAc)Cl(PPh_3)_3]$ in 60% yield which was formulated as (XXXV) or (XXXVI)



(XXXV)



(XXXVI)

based on ^{13}C and ^{31}P spectroscopic characteristics and analytical data. During the reaction, formaldehyde was evolved as detected by use of Brady's solution.

On heating methanolic solutions of $Ru_2(OAc)_4Cl$ and the $-(CH_2)_2PPh_2$ functionalised trisiloxane and polysiloxane, (3) and (14a) respectively, the solution again turned from brown to yellow. In the sensitive test with Brady's solution, small amounts of formaldehyde were again detected. Lack of time prevented more than a cursory investigation of this reaction, but it seems likely that a siloxane supported catalyst could be used for this reaction too

5.3. EXPERIMENTAL

5.3.1. HYDROSILYLATION REACTIONS

All of the hydrosilylation reactions were carried out under a nitrogen atmosphere to prevent hydrolysis of the Si-H bond by atmospheric moisture.

VINYL ENDBLOCKED POLYDIMETHYLSILOXANE - $Me_3SiO[Me_2SiO]_3[MeSi(H)O]_5SiMe_3$ HYDROSILYLATION PRODUCT

A mixture of a vinyl endblocked polydimethylsiloxane (12.9g containing 2 x 10^{-3}mole $-CH=CH_2$) and $Me_3SiO[Me_2SiO]_3[MeSi(H)O]_5SiMe_3$ (0.54g containing 2 x 10^{-3}mole SiH) and the catalyst (1 x 10^{-6}molar) were heated with vigorous stirring until gellation of the reaction mixture occurred, at which point the temperature of the oil bath was noted. Due to the nature of the product (a hard insoluble rubber) no characterisation has been attempted.

$(Me_3SiO)_2Si(Me)(CH_2)_7CH_3$ (69)

A mixture of $(Me_3SiO)_2Si(Me)H$ (2.2g, 10.0mmol) and 1-octene (1.23g,11.0mmol) and the catalyst (5 x 10^{-7} molar) were heated in a tube supported over a solvent of required boiling point (toluene or various alcohols) in order to maintain a constant reaction temperature. The reactions were followed by gas liquid chromatography, and consisted of examining the peak area of either of the olefin or Si-H containing starting materials, which had retention times considerably different from those of the product. Infrared spectroscopy also proved a useful tool in monitoring the progress of the hydrosilylation reactions (loss of ν(SiH) at 2150cm^{-1}). In order to positively identify the products, the catalyst was separated from products using

column chromatography (fluorosil 100-200mesh) with cyclohexane as eluent. The excess solvent and unreacted olefin was removed by pumping in vacuo and the residue was distilled under reduced pressure to yield the silylated product as a colourless oil (data in Table 5.2).

A similar procedure was used for the preparation of $(Me_3SiO)_2Si(Me)(CH_2)_9CH_3$ (70).

5.3.2. OXIDATIVE COUPLING REACTIONS

A mixture of $Me_3SiO[Me_2SiO]_{95}[MeSi\{(CH_2)_3C_6H_3(OH)Me\}]_5SiMe_3$ (4.0g, 0.5mmol) and the catalyst (to give 0.025% metal species in the reactant mixture) in an aluminium dish were heated in an oven in the presence of molecular oxygen until curing had occurred.

5.3.3. DEHYDROGENATION REACTIONS

A solution of $[Ru_2(OAc)_4Cl]$ (0.05g, 0.1mmol) and PPh_3 (0.18g, 0.7mmol) dissolved in anhydrous methanol ($25cm^3$) was heated under reflux. The colour of the solution changed from brown to orange-yellow. The reaction solution was purged with a stream of dinitrogen gas, which was subsequently bubbled through Brady's solution in order to detect formaldehyde. The reaction was repeated but replacing triphenylphosphine with the $-(CH_2)_2PPh_2$ functionalised model siloxane (3) (0.31g, 0.7mmol) or polysiloxane (14a) (1.43g, 0.35mmol). Small amounts of red precipitate were formed in each reaction, indicative of formaldehyde formation.

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Appendix I

SAFETY

The toxicological properties of silanes and siloxanes have not been fully investigated, and necessary precautions were taken when using these materials. The reagents involved in this work are commonly used materials, and the precautions taken when handling them were in accordance with their known hazards.

REAGENTS

All chemicals employed were standard laboratory reagents (BDH or AnalaR grade) which were used without further purification unless otherwise stated. All laboratory solvents with the exception of benzene were dried over BDH 4A molecular sieves for at least 24h., and deoxygenated with oxygen-free dry dinitrogen gas prior to use. Acetone was distilled from anhydrous calcium sulphate, while benzene was dried over sodium wire. Diethyl ether and tetrahydrofuran were freed from peroxides by passing through an alumina column. Diethyl ether and dichloromethane were distilled from calcium chloride, and tetrahydrofuran from calcium hydride.

All siloxane containing materials were provided by Dow Corning Limited and where appropriate, were purified by distillation under reduced pressure. Dichloromethylvinylsilane, $SiMeCl_2(CH=CH_2)$, was commercially available from Aldrich Chemical Company, and was used as received.

APPENDIX II

INSTRUMENTATION

ANALYSES

Carbon, hydrogen, nitrogen and bromine analyses were determined by microanalytical techniques care of Butterworth Laboratories, Teddington, Middlesex, and latterly by the Analytical Services, School of Chemistry, University of Bath.

INFRARED SPECTROSCOPY

Infrared spectra were recorded on either a Perkin-Elmer 577b or 599b spectrophotometer in the region 4000-200cm^{-1}. Samples were prepared as neat oils or nujol mulls using NaCl discs, or as solutions in cyclohexane in a Beckmann RIIC FS 125 0.1mm NaCl cell. Samples were held between CsI discs for measurements in the far-infrared region (600-200cm^{-1}).

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

^{1}H (Proton) and ^{13}C (Carbon)

Samples were prepared using deuterated chloroform as solvent unless otherwise stated, with tetramethylsilane or deuterated benzene as internal standards. ^{1}H-nmr spectra were recorded routinely on a Hitachi Perkin-Elmer R-24B (60MHz) or a JEOL PS100 spectrometer. ^{13}C-nmr spectra were recorded on a JEOL FX90Q FT nmr spectrometer. Towards the end of these studies, ^{1}H- and ^{13}C-nmr spectra were recorded on a JEOL GX 270 instrument (operating at 67.80 MHz for ^{13}C measurements)

^{29}Si (Silicon) and ^{31}P (Phosphorus)

^{29}Si- and ^{31}P-nmr spectra were recorded using a JEOL GX 400 spectrometer housed at the Department of Chemistry, University of Bristol

The samples were dissolved in deuterochloroform, with tetramethylsilane and H_3PO_4 as internal standards for ^{29}Si- and ^{31}P-nmr spectra respectively.

Gel Permeation Chromatography (GPC)

AnalaR toluene was used as solvent, the sample concentration being dependent upon sample solubility. Molecular weight determinations were referenced to polystyrene standards, analysed under the same physical conditions. GPC studies were carried out on a Knauer HPLC pump (Type 64.00) and a Knauer Differential Refractometer for analytical and semi-preparative use (No. 98). Analytical studies were performed using 30cm PL-Gel 5m mix and 10m mix columns,with preparative runs on a 60cm PL-Gel 10m mix column. The flow rate for analytical studies was 1ml min^{-1} with injection volumes of 10µl for sample concentrations of 5%^{w}/w. For preparative work, the flow rate was 9.9ml min^{-1} with injection volumes of 2000µl.

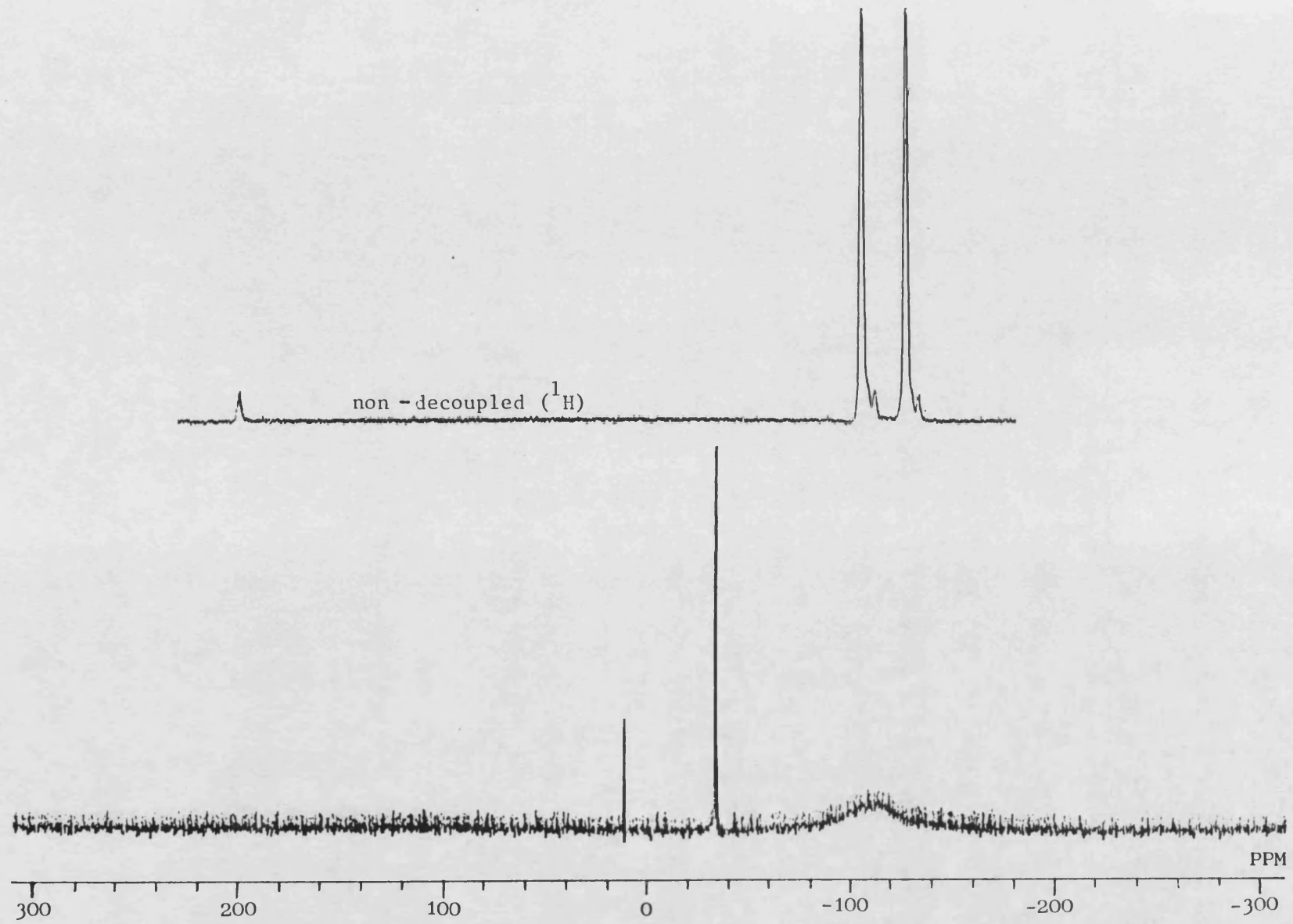
GAS CHROMATOGRAPHY (GC)

GC studies were carried out on a Pye Unicam Series 104 chromatograph (FID detector). Injection volumes were 5µl. Flow rates were N_2 15Psi, H_2 16Psi and air 7Psi. Column, injection and detector temperature were all 130^{o}C.

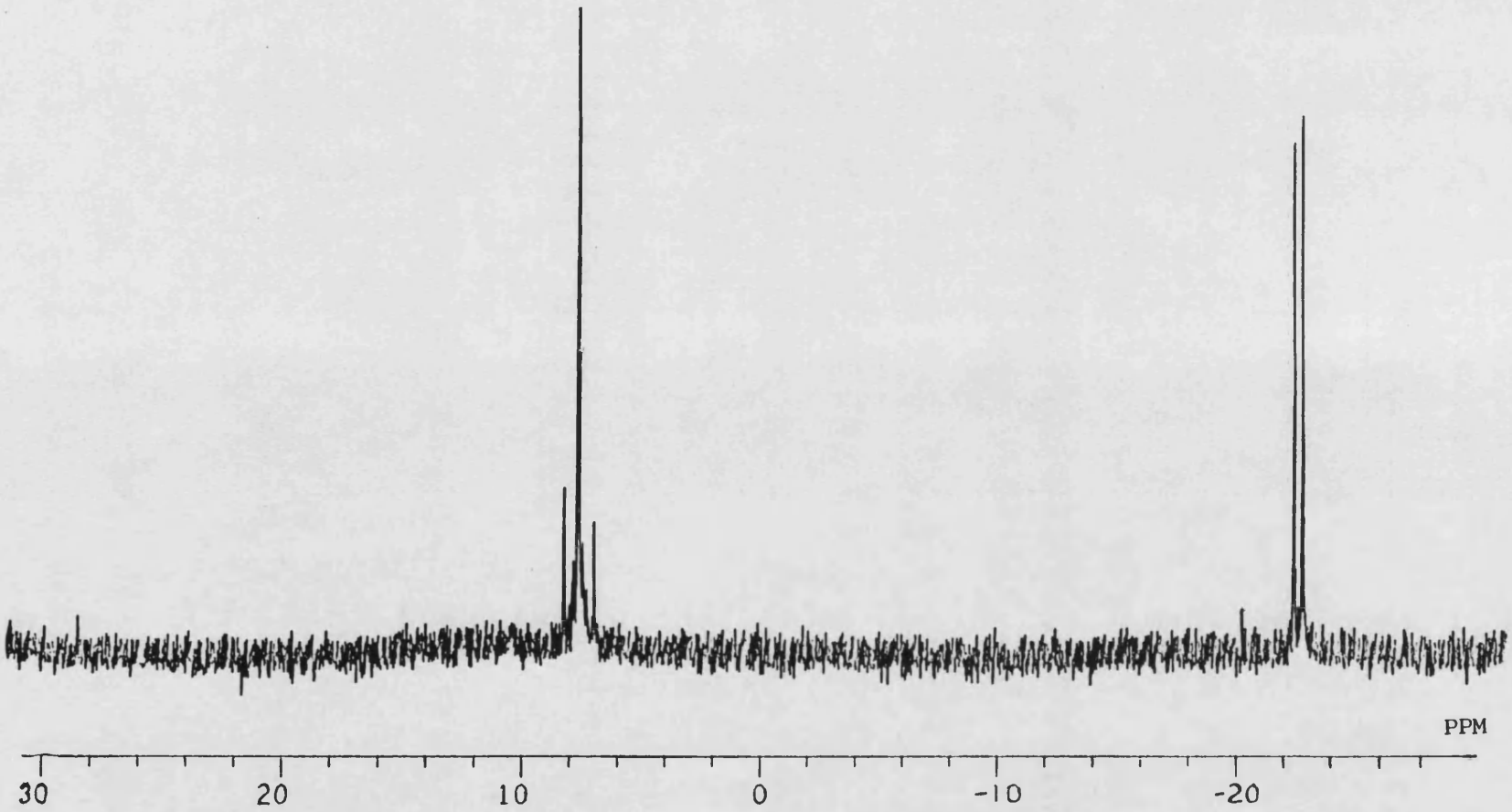
REFLECTANCE/UV (VIS) SPECTROSCOPY

Solution measurements (in cyclohexane or dichloromethane) were carried out on a Cecil CE595 Double beam digital UV spectrophotometer. Reflectance spectra were ran as neat samples on a Perkin Elmer 330 instrument.

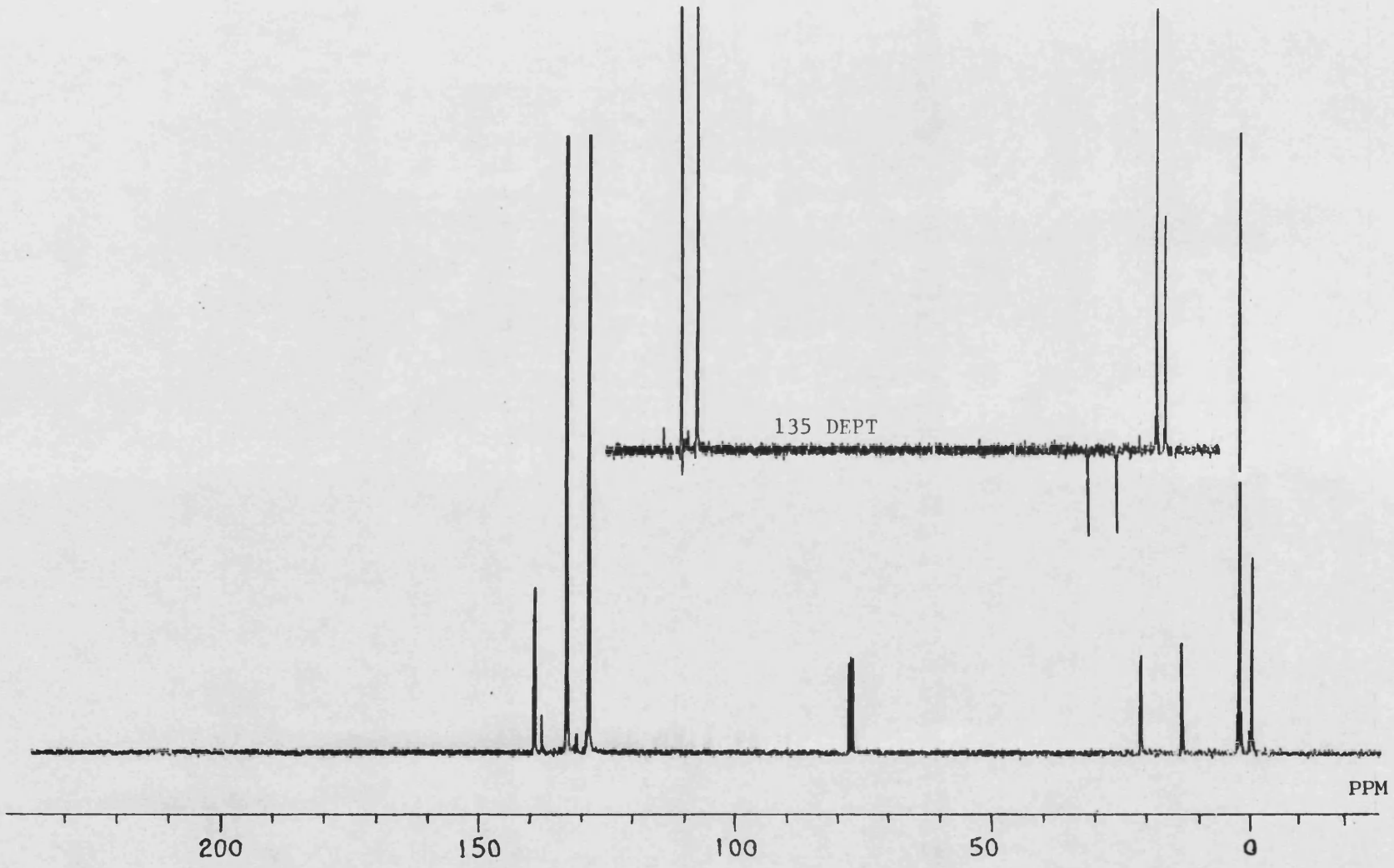
^{29}Si-nmr spectrum of $(Me_3SiO)_2Si(Me)H$ (1)



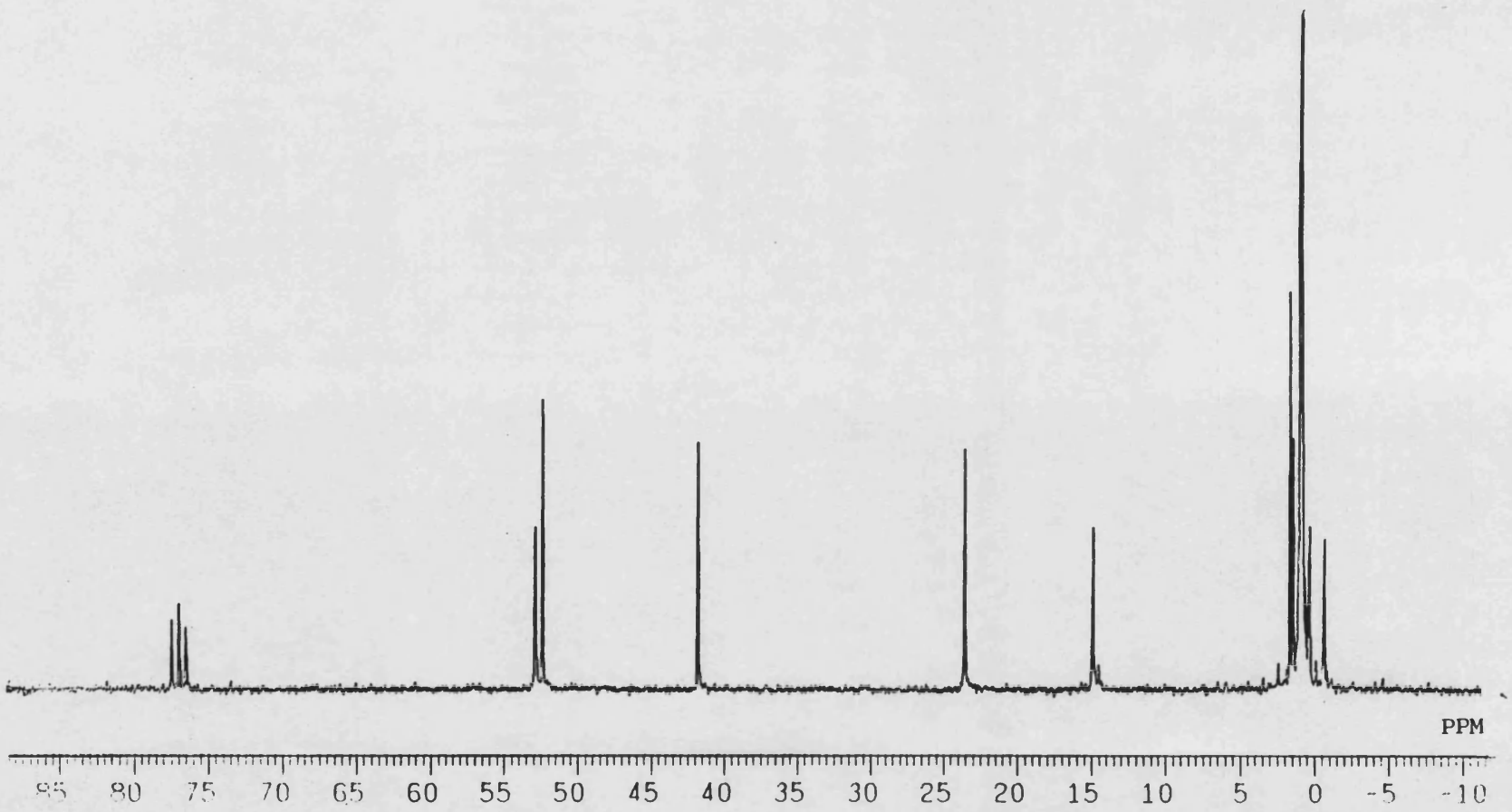
^{29}Si-nmr spectrum of $(Me_3SiO)_2Si(Me)CH_2CH_2PPh_2$ (3)



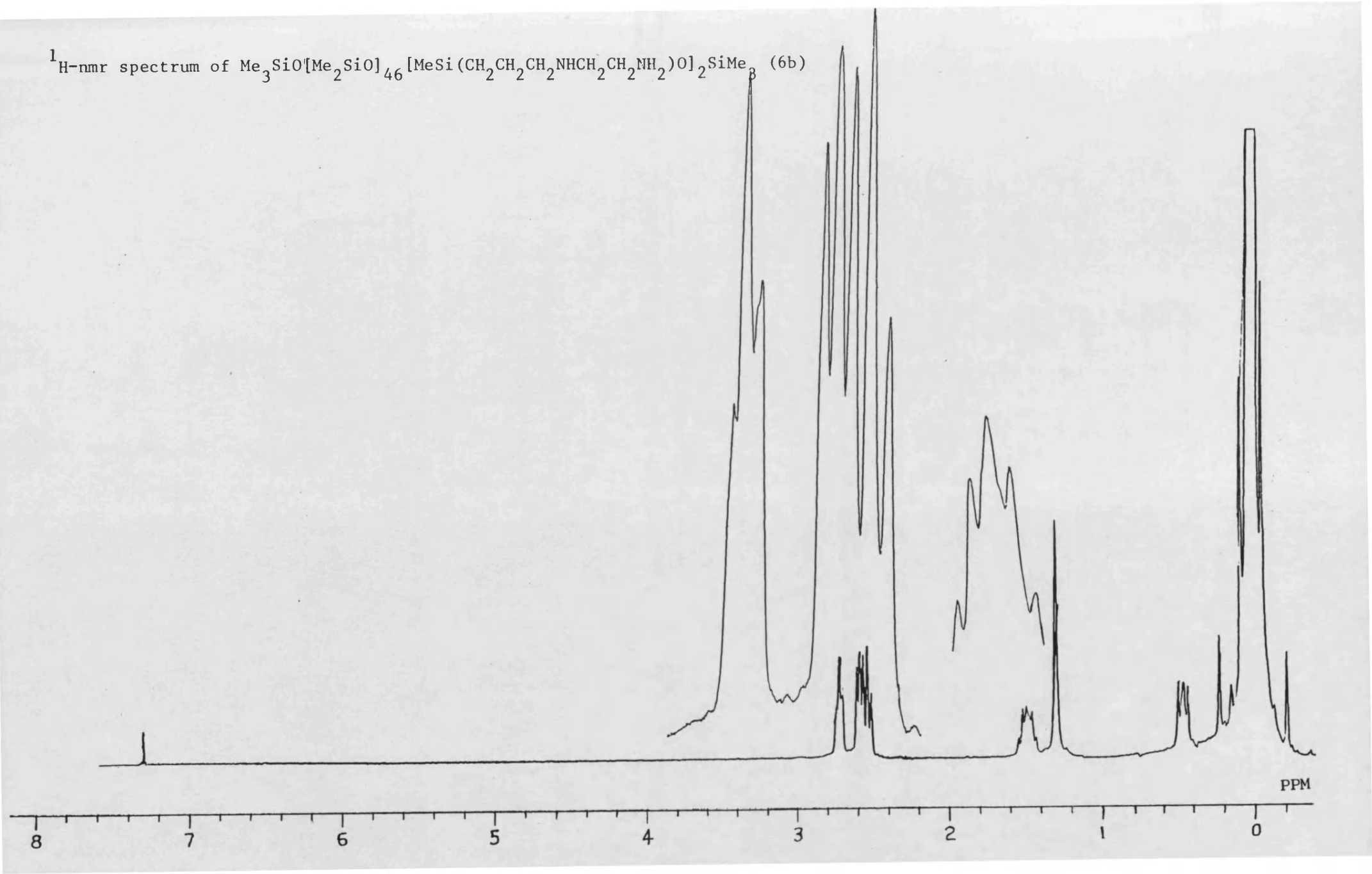
^{13}C-nmr spectrum of $(Me_3SiO)_2$ Si(Me)CH_2CH_2SPh (4)

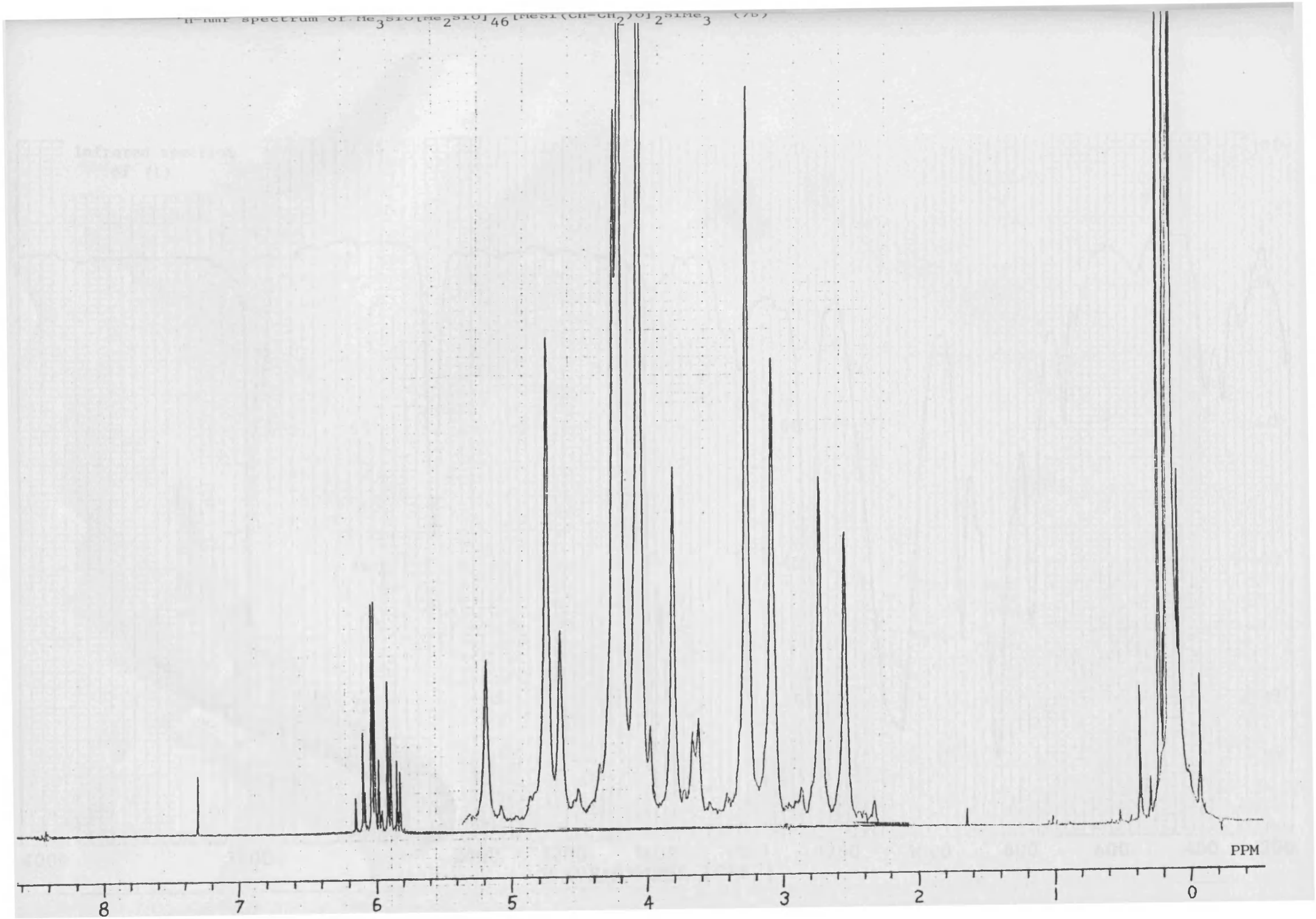


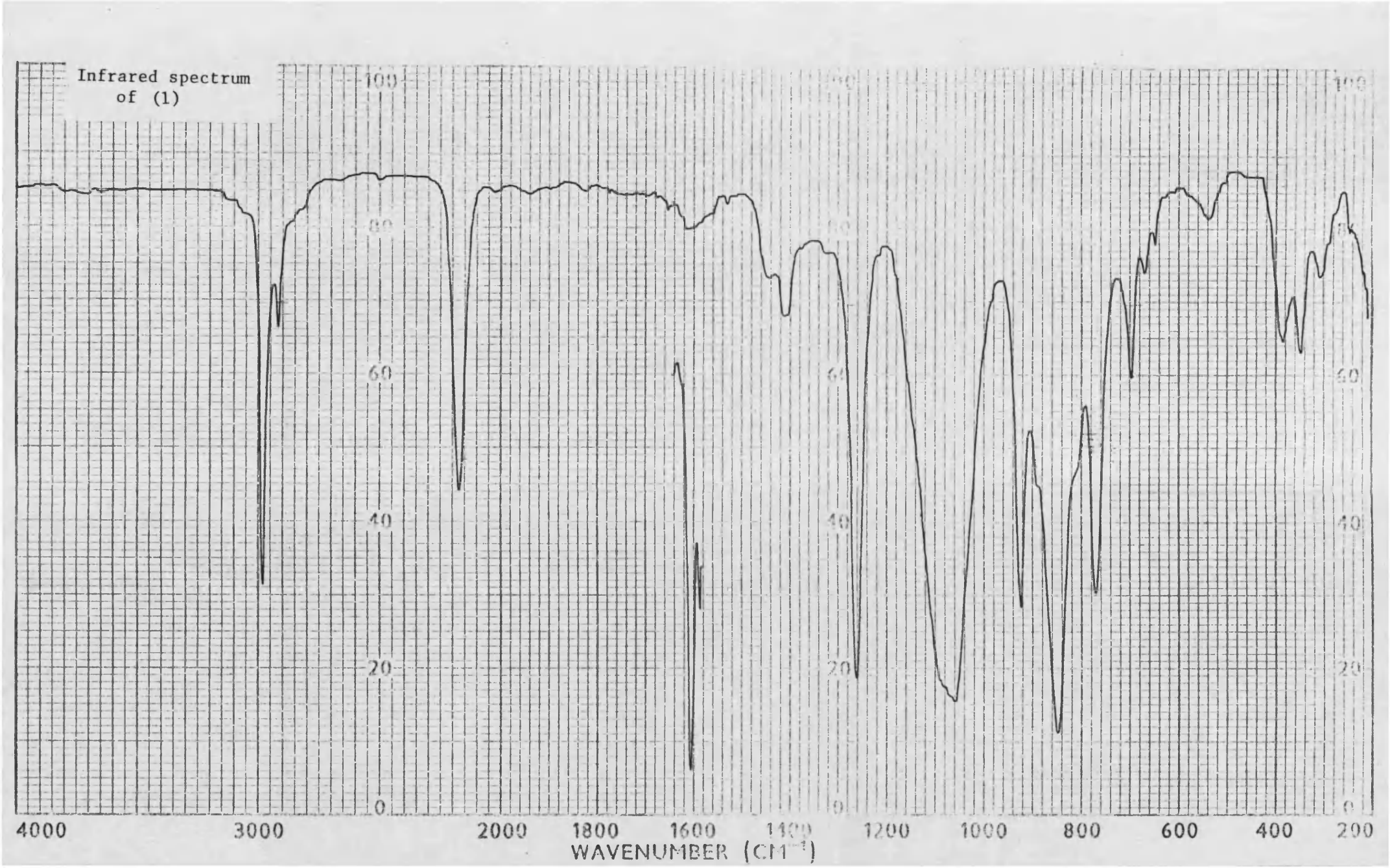
^{13}C-nmr spectrum of $Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2CH_2NHCH_2CH_2NH_2)O]_2SiMe_3$ (6b)

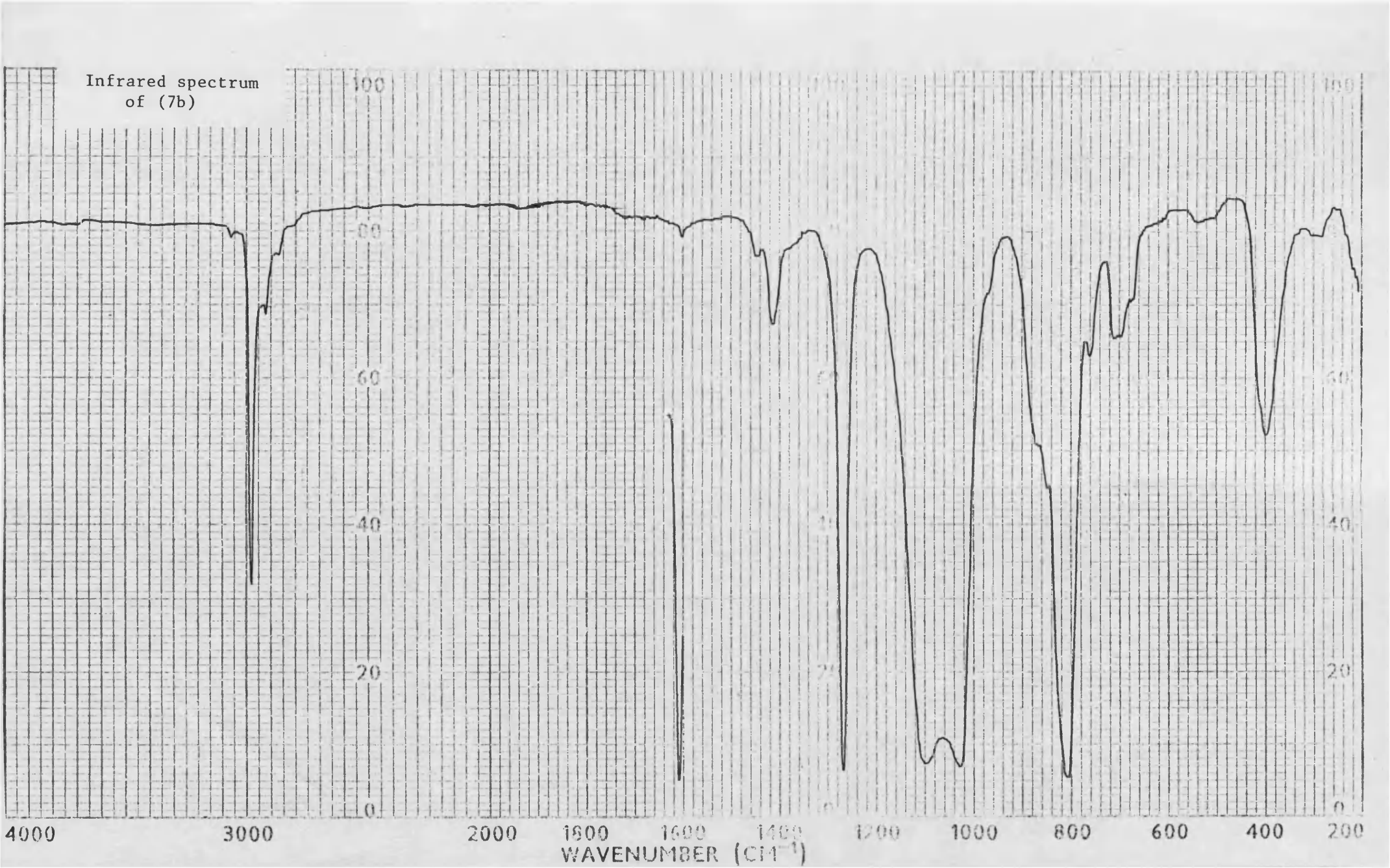


^{1}H-nmr spectrum of $Me_3SiO[Me_2SiO]_{46}[MeSi(CH_2CH_2CH_2NHCH_2CH_2NH_2)O]_2SiMe_3$ (6b)

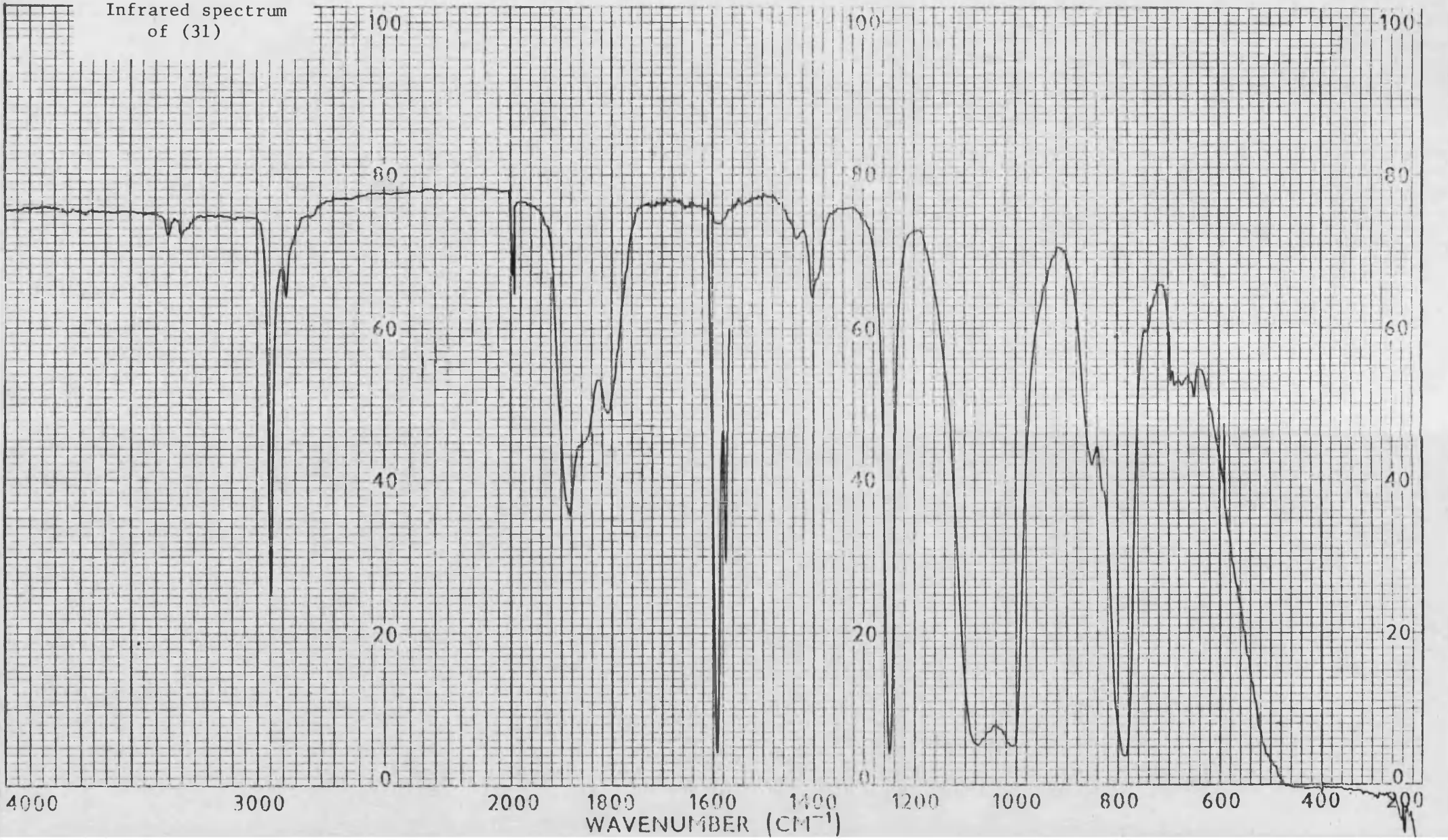


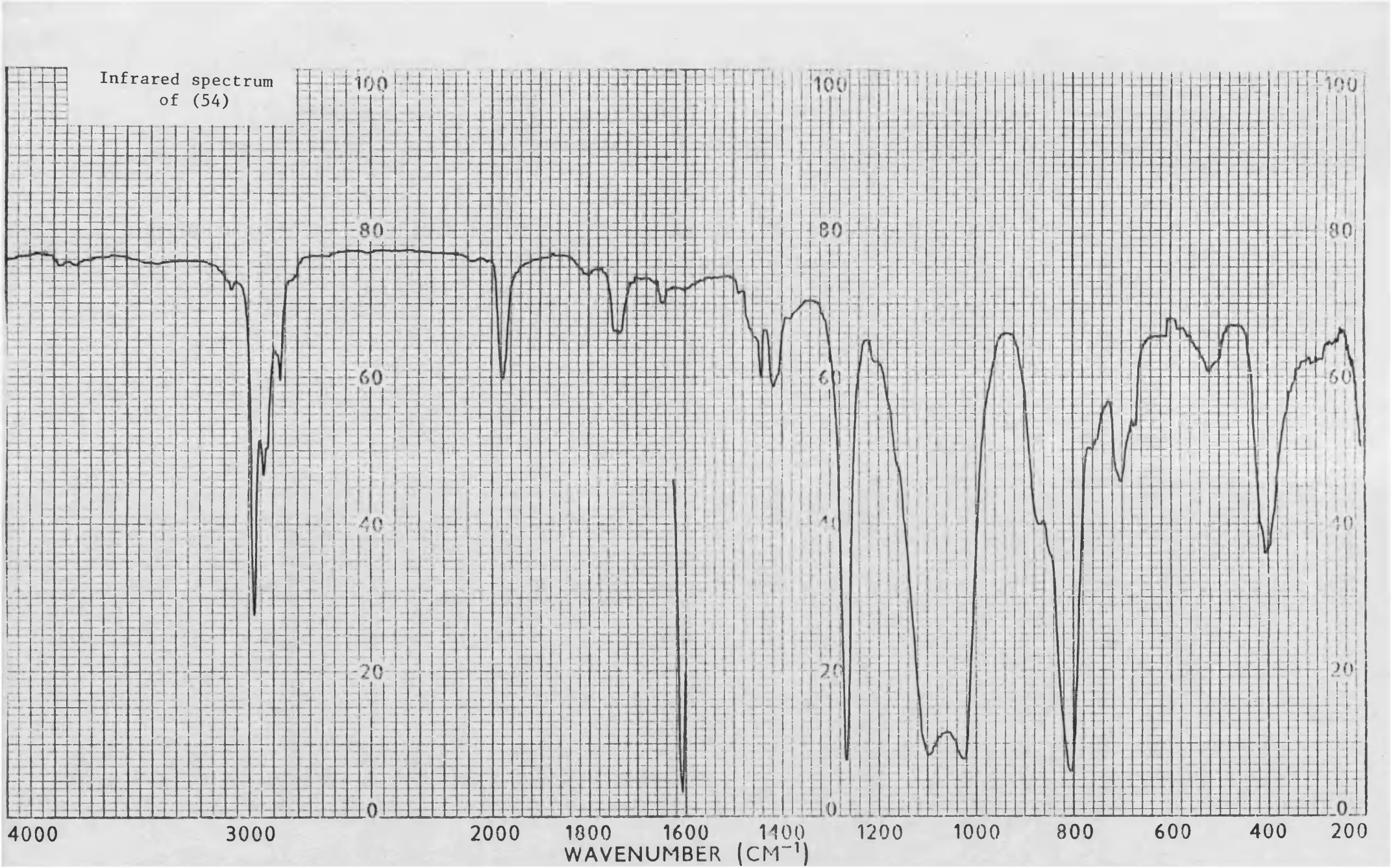

PPM
8
7
6
5
4
3
2
1
0


Infrared spectrum
of (1)
100
80
60
40
20
0
4000
3000
2000
1800
1600
1400
1200
1000
800
600
400
200
WAVENUMBER (CM⁻¹)


Infrared spectrum
of (7b)
100
80
60
40
20
0
4000
3000
2000
1800
1600
1400
1200
1000
800
600
400
200
WAVENUMBER (CM⁻¹)

Infrared spectrum of (31)




Infrared spectrum
of (54)
100
80
60
40
20
0
4000
3000
2000
1800
1600
1400
1200
1000
800
600
400
200
WAVENUMBER (CM⁻¹)